THE DETERMINATION OF BORON IN STEELS

A thesis submitted by

DAVID J. DONNELLY M.Sc., C.Chem., MRSC.

In part fulfilment for the degree of

Doctor of Philosophy

of the

Council for National Academic Awards

Sponsoring Establishment

The Polytechnic, Wolverhampton

December 1987

THE DETERMINATION OF BORON IN STEELS

by D.J. Donnelly

ABSTRACT

A method for the rapid determination of boron in mild and low alloy steels containing 0.0005 to 0.010%B has been developed based on the reaction of 1-(arsenophenylazo)-2-hydroxynaphthalene-3, 6-disulphonic acid trisodium salt (Thoron) with boric acid in sulphuric acid (90% v/v) to produce a fluorescent complex. The method is compatible with dissolution techniques used for the separation of 'soluble' and 'insoluble' boron and was found to be tolerant to the presence of iron and other elements at the levels commonly present in steel. The procedure was automated using the AutoAnalyzer system. The reproducibility at 0.002%B is better than $\pm$0.0001%B. The limit of detection is less than 0.0005%B.

The composition and stability of the complex between boric acid and thoron were determined from fluorescence measurements. Only a single complex between one boric acid and one thoron molecule was found. The apparent stability constant in 90% v/v sulphuric acid and at 25°C was found to be $7 \times 10^3\ M^{-1}$.

^{11}B n.m.r. spectroscopy showed that at least two borate anions were found to be present in solutionsof H_3BO_3 in concentrated sulphuric acid, $B(HSO_4)_4^-$ appeared to be the predominant species. While in less concentrated acid this species was in equilibrium with rapidly interconverting tetrahedral species of the form $B(OH)_x(HSO_4)_{4-x}^-$. ^{11}B n.m.r. has also been used to determine the stability constants of the thoron - boric acid complex and other similar tetrahedrally coordinated boron complexes with a range of 2-hydroxyphenylketones and mono-phenylazochromotropic acid derivatives. These values are consistent with those derived from fluorescence measurements.

ACKNOWLEDGEMENTS

The author thanks Dr D.A.E. Rendell for his advice and direction over the many years this work has taken. The author is also grateful to Dr B.W. Rockett, Dr J.D. Hobson; to SERC for allocation of time on the high field n.m.r. service and to Dr E. Curzon at Warwick University for assistance in the running of the spectra.

The author acknowledges his ex employers Round Oak Steel Works Limited and Round Oak Laboratories Limited for their contributions to the tuition fees and use of facilities.

CONTENTS

1. INTRODUCTION

The principal reason for adding alloying elements nickel, chromium and molybdenum to steel is to improve its hardenability, that is the depth of hardening which can be achieved when the hot steel is rapidly cooled in water, oil or even air.

Shortly before the Second World War it was noticed, quite accidentally, that an appreciable increase in hardenability occurred in steel treated with complex deoxidizers during manufacture. Minute traces of boron increased the hardenability many hundreds of times more effectively than nickel, chromium or molybdenum.

The need to conserve strategic raw materials during the war led to successful use of boron treated steels in America as a substitute for alloy steels. In recent years the economy of using boron steels has become obvious as the cost of nickel and molybdenum increase.

The production of high strength fasteners demands a balance between ductility and high hardenability. Those alloys added to increase hardenability also tend to reduce ductility. Boron additions not only have minimal effect on ductility, but also greatly increase hardenability

1.1 Hardenability - The effect of Boron Additions

The formal definition of hardenability is the capacity of a steel to transform, partially or completely, from austenite (γ - iron) to a given percentage of martensite (a stressed form

of α- iron supersaturated in carbon - the hardest constituent obtained in a steel) at a given depth below the surface when cooled under the given conditions.

The transformation of austenite into its decomposition products of 'ferrite' and carbide (Figure 1.1), depends on nucleation and growth, a time dependent process. To produce martensite the formation of which is temperature dependent, it is necessary to cool the austenite rapidly enough to prevent the nucleation of ferrite and carbide aggregates. The presence of boron suppresses the start of the transformation to ferrite and carbide by segregating to the austenite grain boundaries favouring the production of martensite and the consequent enhancement of hardenability (1).

The effects of boron are unique in several respects - an extraordinarily small amount has a large effect on hardenability - the effect varies notably with carbon content of the steel - and there are other definite influences on the effectiveness of boron, such as the nitrogen content of the steel.

Kapadia et al.(2) related hardenability to an 'effective' boron content obtained from the interactive effect of boron with titanium and zirconium added to control nitrogen in steel (Figure 1.2). A maximum hardenability (an increase of 2.8 times) was obtained at about 0.001% 'effective' boron. Lewellyn and Cook (3) also found a maximum hardenability effect when 'soluble' boron was at or below 0.001%. Melloy et al.(4) derived boron multiplying factors in terms of total boron content (Figure 1.3), the maximum occurring at 0.002% total boron.

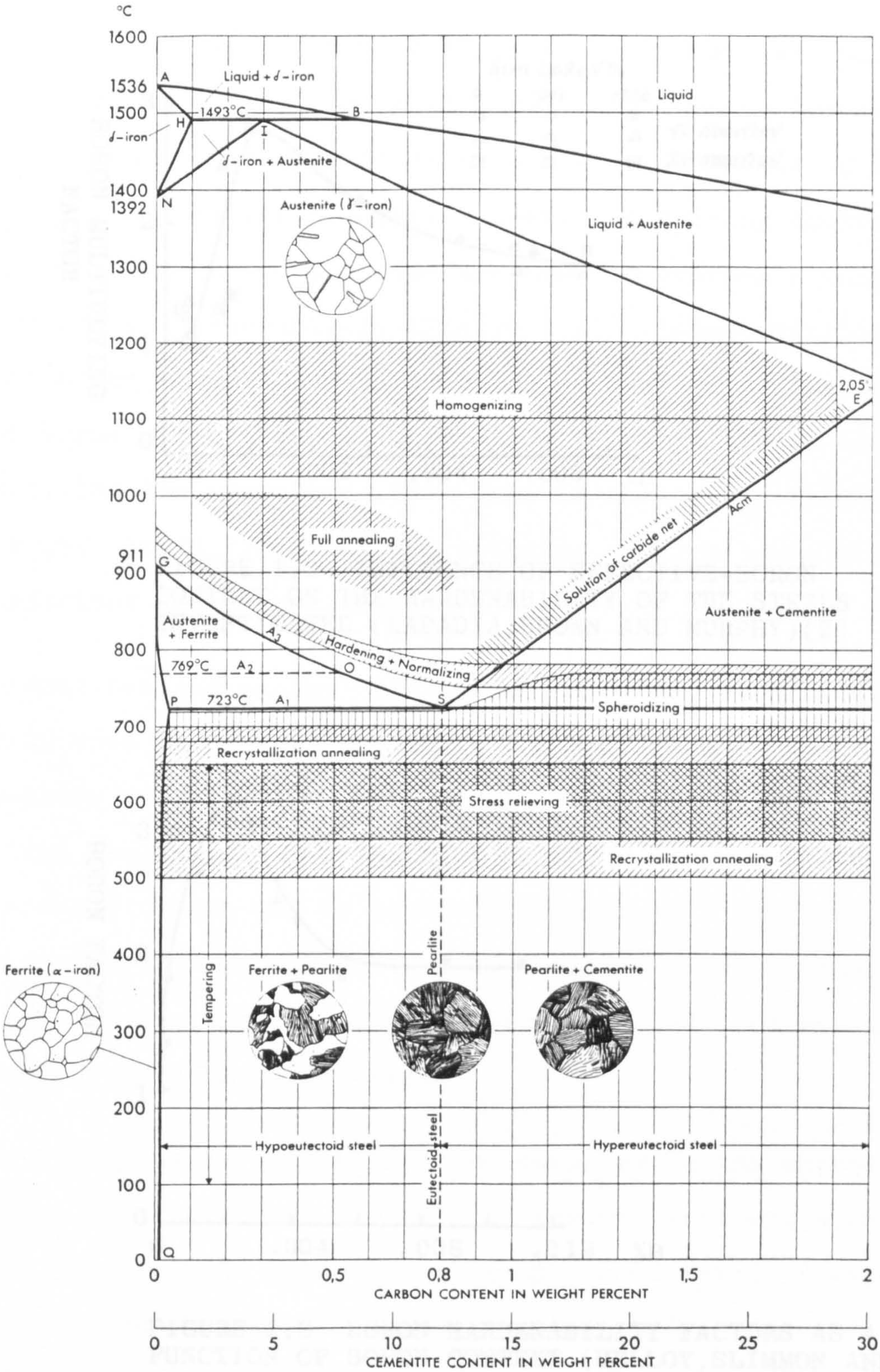


FIGURE 1.1 IRON - CARBON EQUILIBRIUM DIAGRAM (STEEL PART)

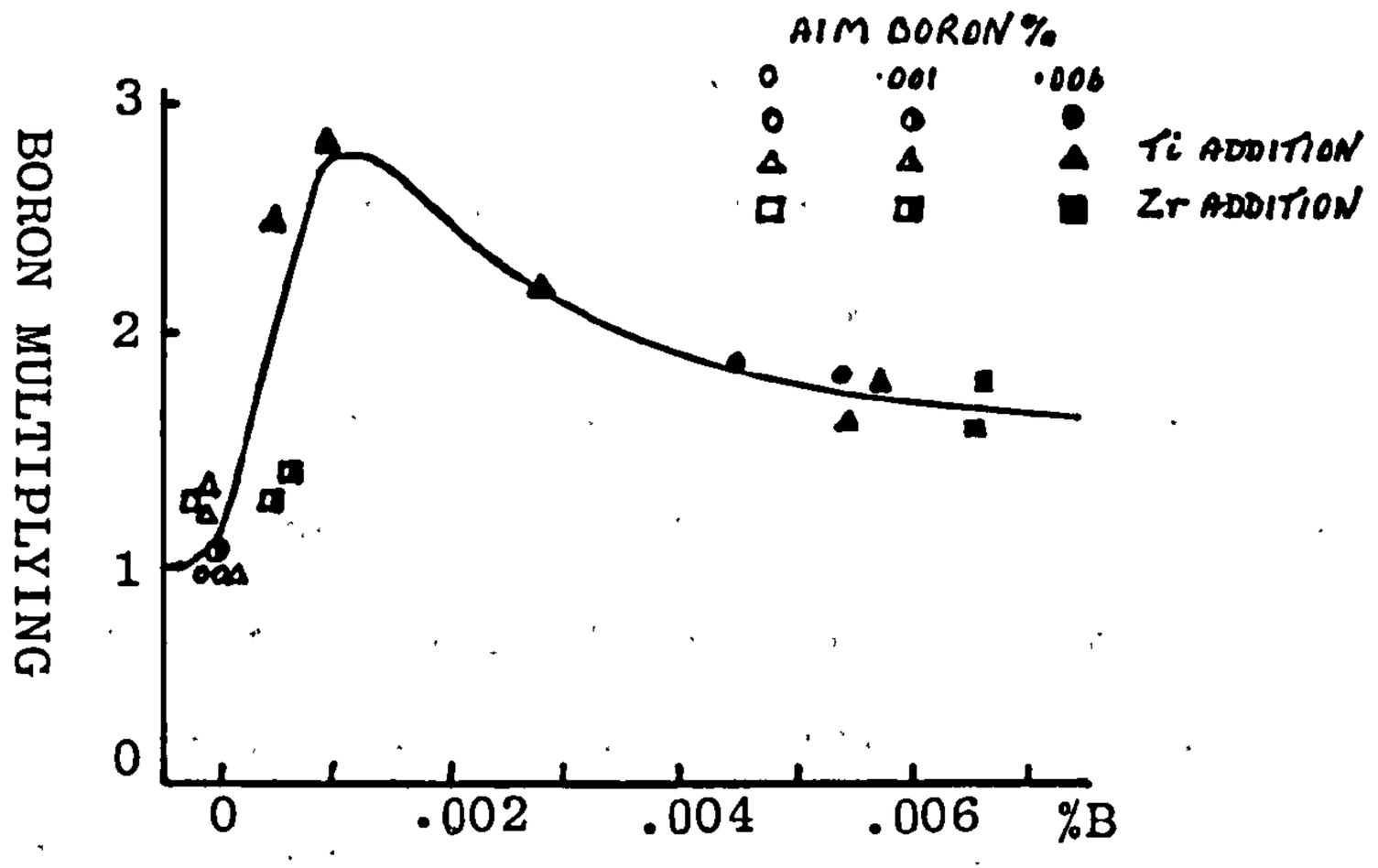


FIGURE 1.2 INFLUENCE OF EFFECTIVE-BORON CONTENT ON THE HARDENABILITY OF THE STEELS INVESTIGATED (KAPADIA,BROWN AND MURPHY)(2)

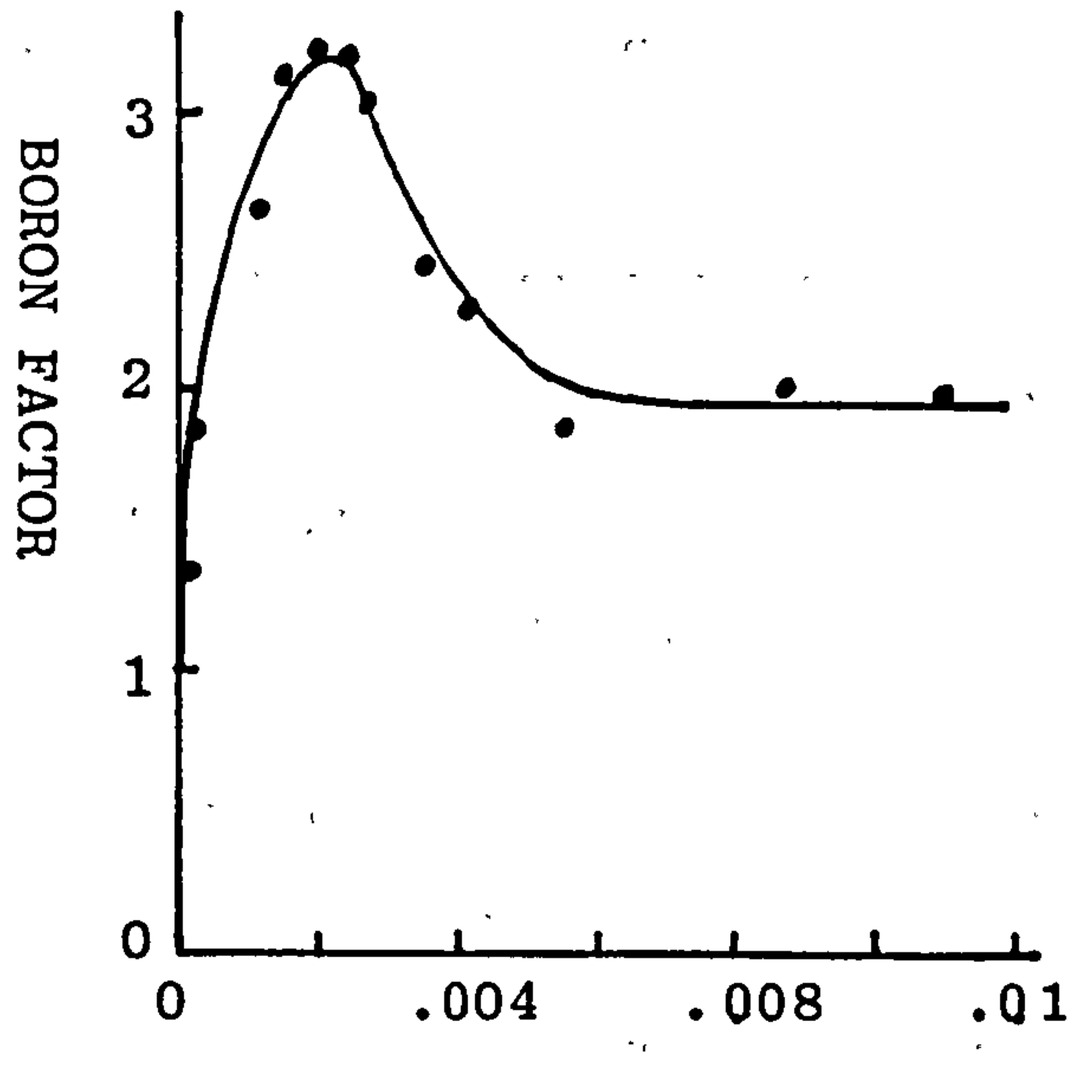


FIGURE 1.3 BORON HARDENABILITY FACTORS AS A FUNCTION OF BORON CONTENT (MELLOY,SLIMMON AND PODGURSKY)(4)

1.2 Soluble and insoluble boron

In order to be effective boron must be present as 'soluble' (that is metallurgically soluble) boron. It must be 'protected' by suitable melting and addition practice and also during heat treatment. Complex boron addition agents containing controlled amounts of titanium or zirconium are used to provide a consistent boron effect on hardenability (Figure 1.4). Boron additions 'protected' by aluminium tend to fade (ie. suffer an irreversible loss of boron effectiveness) on heating the steel above normal austenitizing temperatures. This loss is related to diffusion of nitrogen within the steel and reaction to form 'insoluble' boron nitrides and carbonitrides (5).

Direct reading vacuum-ultraviolet emission spectroscopy is routinely used to monitor the boron concentration during the steel making process. The foregoing discussion, however, has shown that the desired mechanical properties are associated with 'soluble' boron and an estimate of this will provide a closer correlation with the boron hardenability effect than the total boron content, which is the figure obtained from emission spectroscopy using a solid sample.

Metallurgically insoluble boron combined as the unreactive nitride is chemically soluble only by severe treatment such as fuming with sulphuric acid - sodium sulphate mixture. A separation may thus be made by dissolving the steel in dilute mineral acid (usually approximately 4M sulphuric acid) when the acid soluble boron equates to the metallurgically active boron in solid solution in the steel or as metallic borides such as Fe_2B, $Fe_3(B,C)$ and the acid insoluble boron to the metallurgically inactive

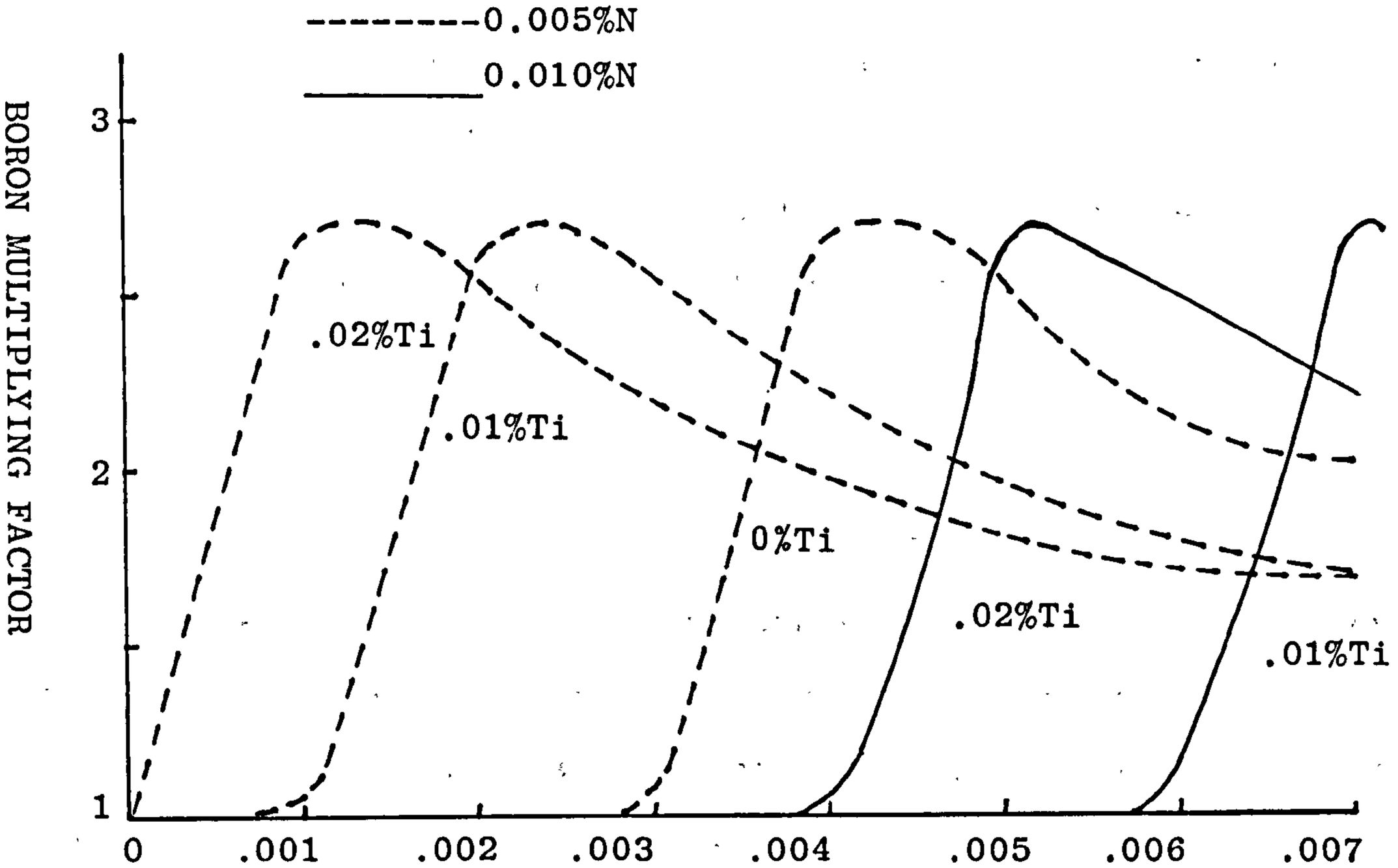


FIGURE 1.4. EMPIRICALLY PREDICTED EFFECT OF BORON ON HARDENABILITY FOR VARIOUS LEVELS OF TITANIUM AND NITROGEN (KAPADIA, BROWN AND MURPHY).(2)

boron in the form of compounds such as BN or non-metallic inclusions (6,7). The insoluble boron may be brought into solution following an alkaline fusion.

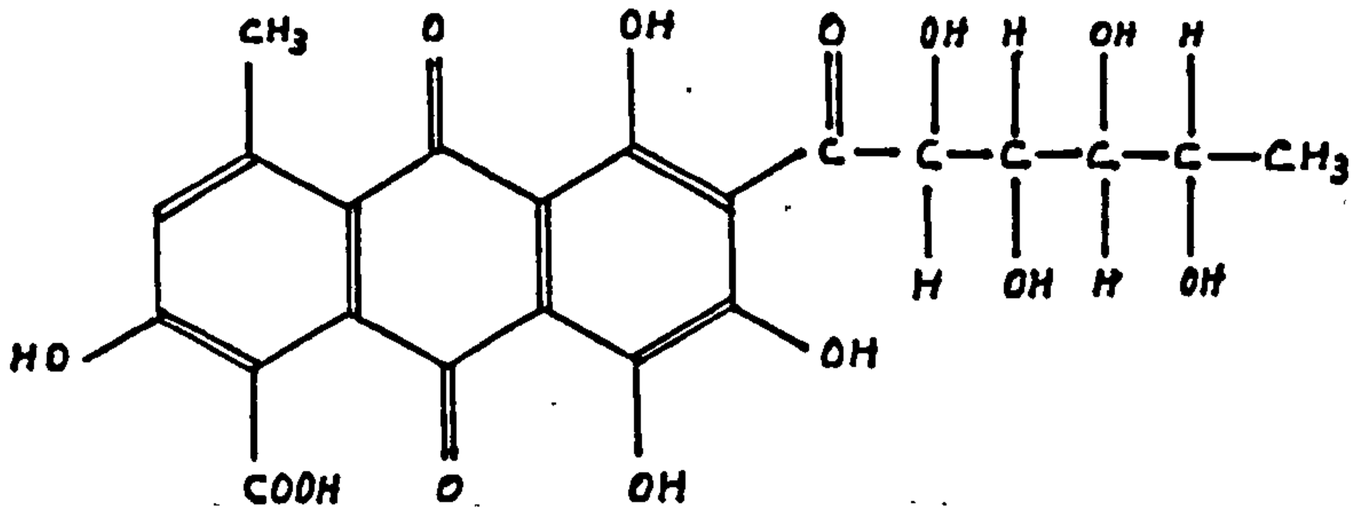
The need for chemical methods of separation of the differing metallurgical forms of boron allows the determination of soluble and total boron contents of treated steels to be advantageously carried out by solution techniques. It is also necessary to use a reliable reference method to analyse the standard steels used for calibrating the routine spectrographic procedures.

1.3 Analysis of boron in solution

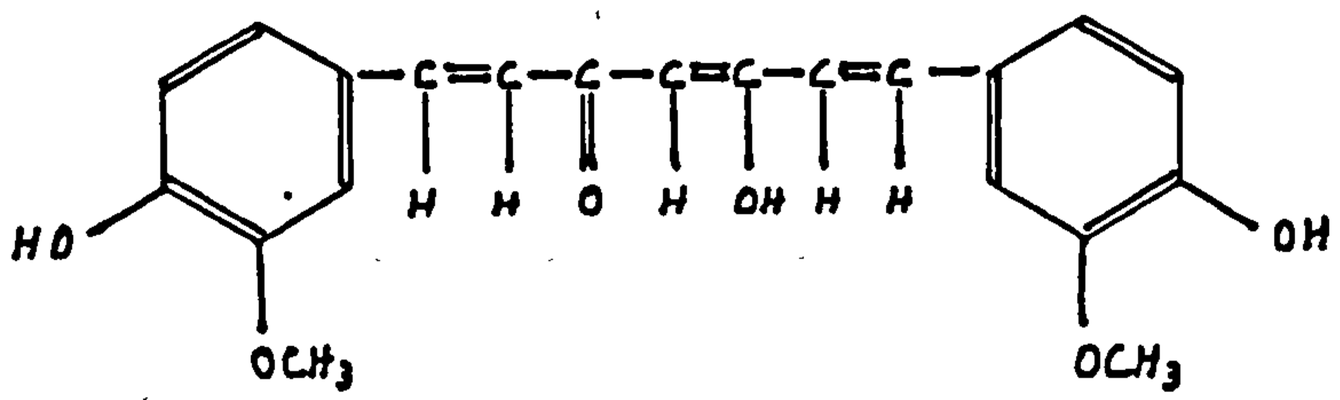
Boron contents of only 0.001 to 0.010% are required to produce the very important metallurgical effects outlined above, this is below the level for satisfactory titration. The methods of adequate sensitivity which meet the general requirements of the steel industry are predominately colorimetric.

1.3.1 Colorimetric methods

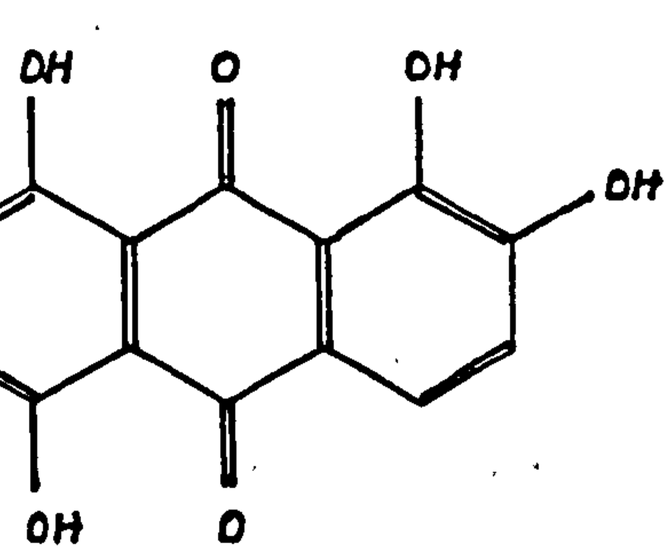
Colorimetric methods have been developed mainly from four reagents and their derivatives. These are carmine, curcumin, quinalizarin and 1,1'-dianthrimide (Figure 1.5). Brande (8) in 1819 stated of boric oxide 'it is very difficultly soluble in water, the solution reddens vegetable blues'. Carmine and curcumin are natural dyestuffs obtained from the cochineal insect and turmeric root and quinalizarin was originally obtained from madder root. All these reagents react with boric acid in strong sulphuric acid, give high back-



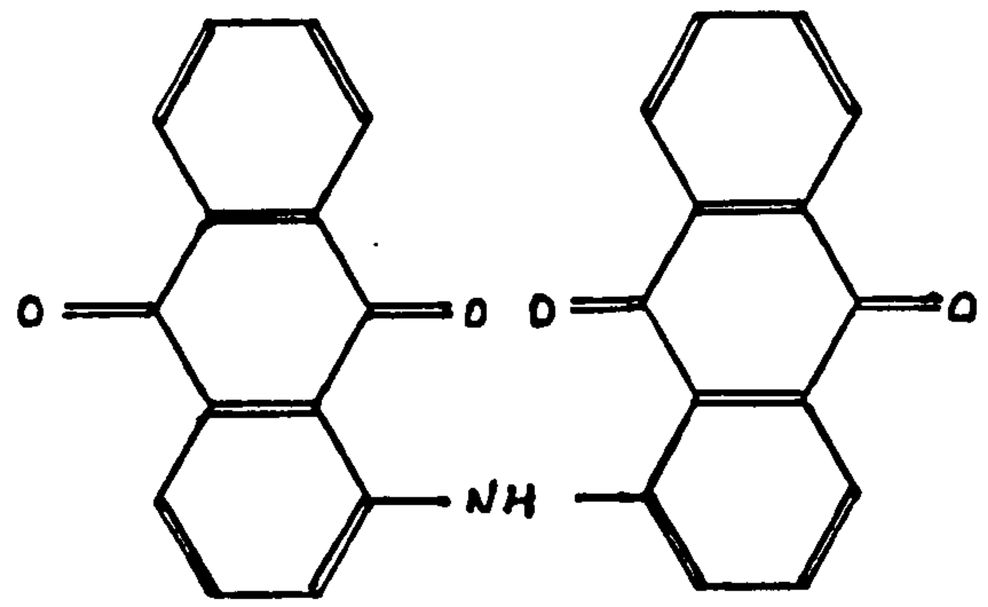
CARMINE



CURCUMIN



QUINALIZARIN



1:1' DIANTHRIMIDE

FIGURE 1.5 PRINCIPAL COLOUR REAGENTS FOR DETERMINATION OF BORON

ground colours and are subject to many interferences. The relative sensitivites of the four reagents have been discussed by Goward and Wiederkehr (9) who found that the Hayes and Metcalfe (10) modification of the curcumin method provided the highest effective molar extinction coefficient (Figure 1.6)

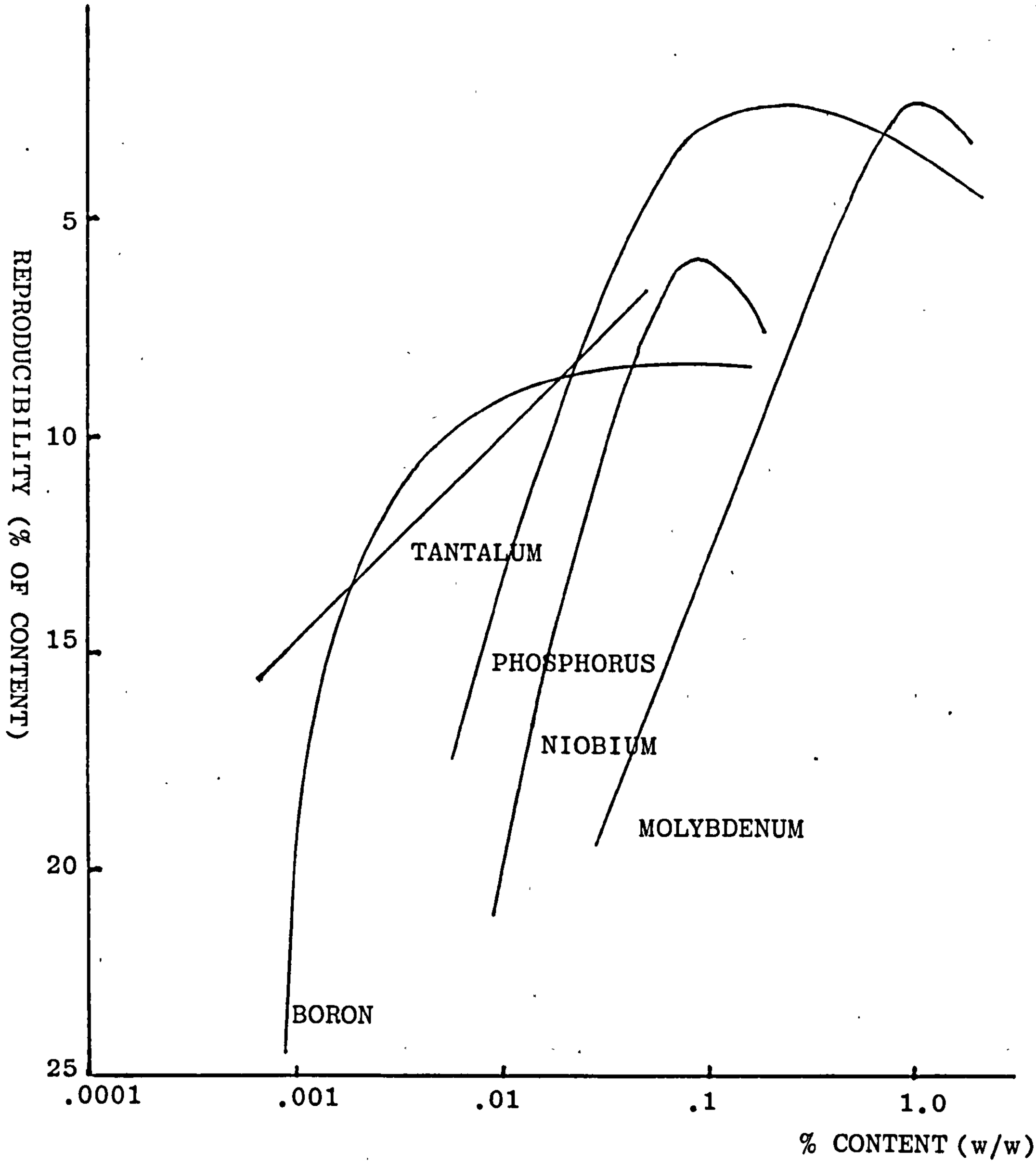
Reagent	Molar extinction coefficient $\varepsilon/10^3$
Quinalizarin	2.7 - 7.0
Carminic Acid	2.1 - 6.5
1,1'-Dianthrimide	12 - 18
Curcumin	151

Figure 1.6 Relative sensitivities of principal colour reagents for boron

In 1967 this method was adopted as a British Standard (11). It was coupled to the old established procedure for separation of boron by distillation of the methyl ester of boric acid (12,13) from quartz apparatus, so that the colorimetric finish is unaffected by alloying elements in the steel. This results in a lengthy procedure and gives results of relatively poor precision compared to British Standard Methods for other elements in steel (Figure 1.7)

Other colorimetric methods have been based on the reaction of the tetrafluoroborate ion. Bode and Fernando (14) used methylene blue for the analysis for boron in steel, extracting the complex in 1,2-dichloroethane. Pasztor and Bode (15) studied seven substituted thionine dyes and examined more than thirty solvents as extraction media for the complex from the surplus dye. Hobson (16) using their method found calibration graphs far from linear with hours being required for separation of solvent and

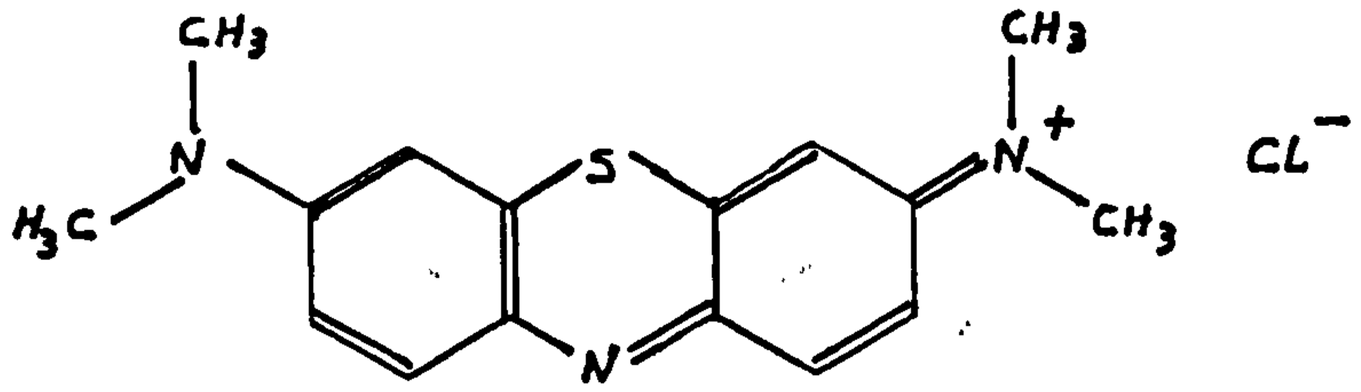
FIGURE 1.7 *PRECISION* OF COLORIMETRIC BRITISH STANDARD METHODS FOR THE ANALYSIS OF STEEL (11)



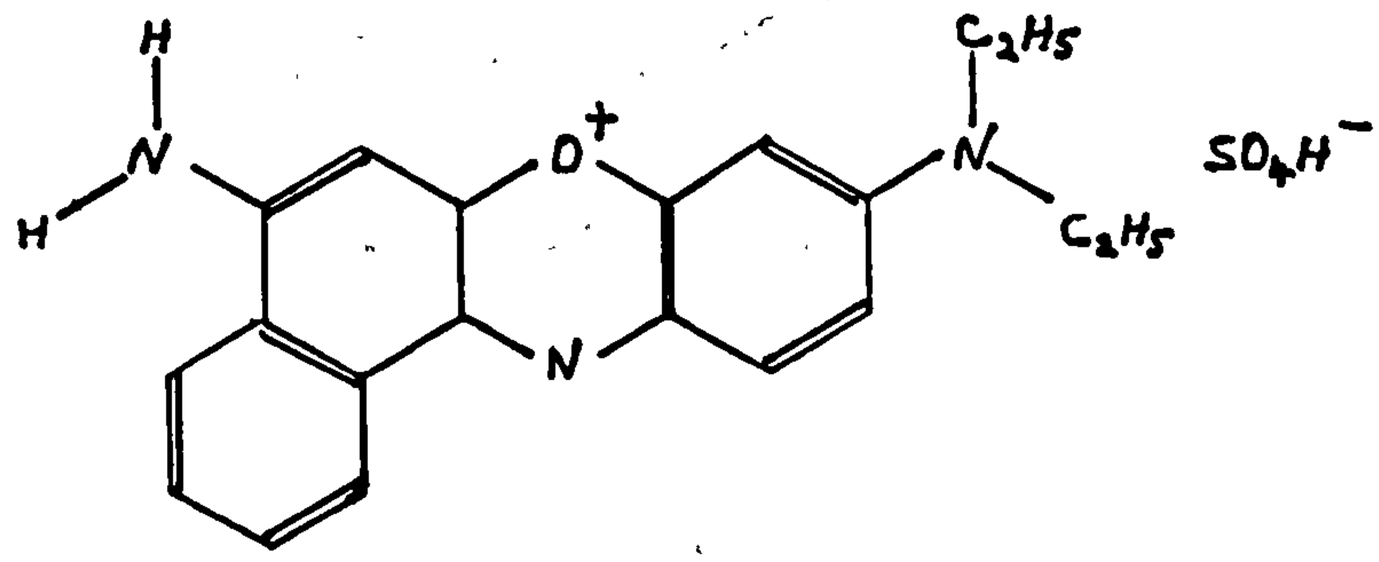
aqueous phases at room temperature. Several interferences were found with metals forming complex ions in hydrofluoric acid solution. Similar methods have been based on the extraction of fluoroborate with oxazine dye stuffs (17) (Figure 1.8).

Dyes based on phenylazo derivatives of chromotropic acid (1,8-dihydroxynaphthalene-3,6-disulphonic acid) have also been used for colorimetric determination of boron. Several workers have used the reaction of chromotrope 2B (Figure 1.9) in sulphuric acid or sulphuric/acetic acid - acetic anhydride mixture. Golubtsova (18) applied the method to complex alloys, separating interfering ions with mercury cathode electrolysis. Green (19) developed a colour in aqueous solution with chromotropic acid itself but also needed to separate interferences by electrolysis. Capelle (20) in an attempt to find a reagent for the determination of boron in aqueous solution examined six phenylazo and imino complexes of H-acid (1-amino-8-hydroxy-naphthalene-3,6-disulphonic acid). Azomethine H (Figure 1.9) gave the best results when applied to the determination of boron in steel, but required several hours for colour development and also removal of iron interference by ion exchange.

It is evident that colorimetric reagents for the determination of boron in steel have been widely, if not exhaustively, studied in attempts to develop more specific and sensitive methods. The majority of the procedures proposed for the determination require colour development in strongly acidic media and/or separation of boron from the iron matrix.

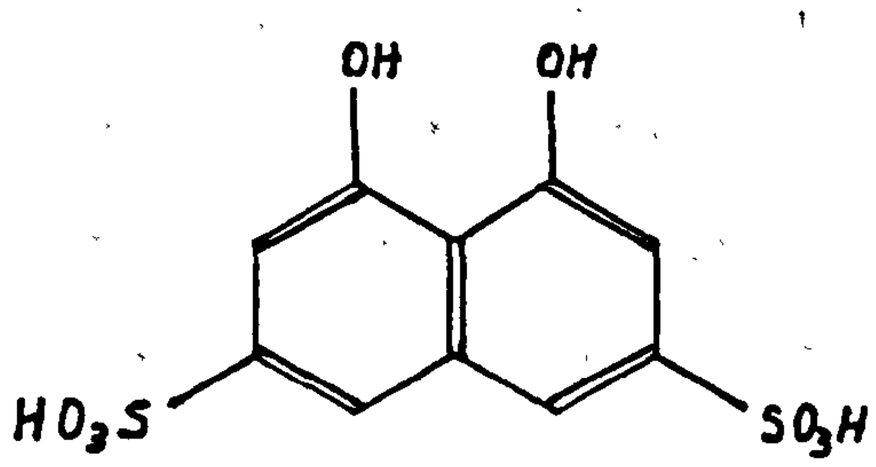


METHYLENE BLUE

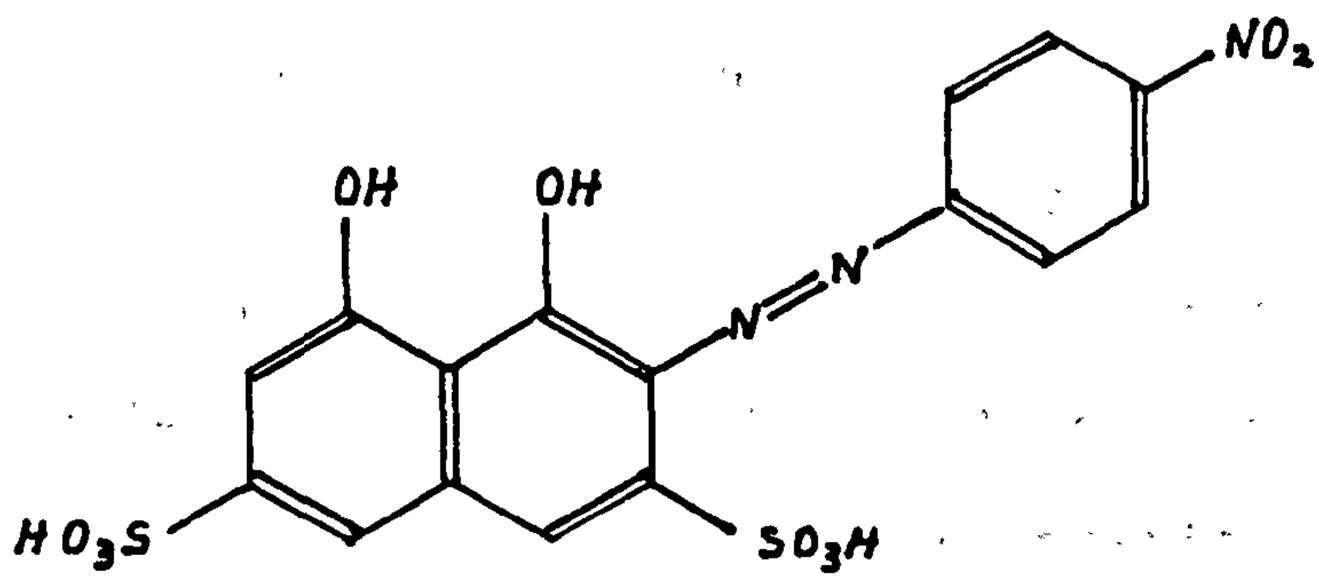


NILE BLUE A

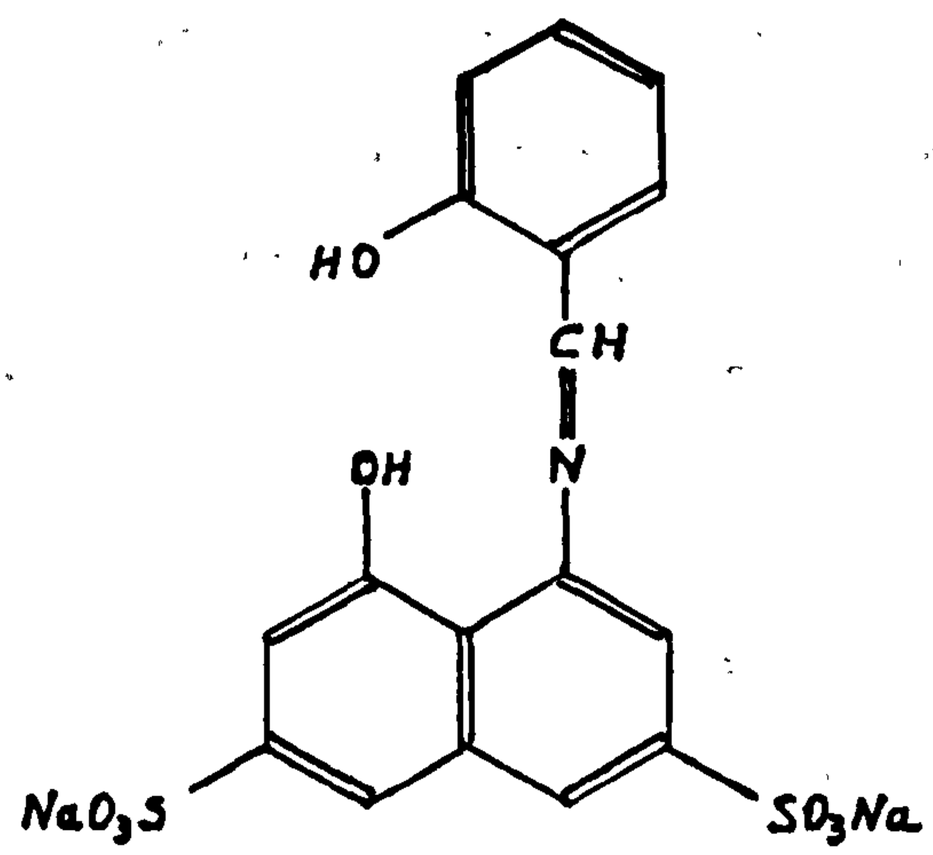
FIGURE 1.8 THIONINE AND OXAZINE DYES REACTING WITH FLUOROBORATE ION



CHROMOTROPIC ACID



CHROMOTROPE 2B



AZOMETHINE H

FIGURE 1.9 COLORIMETRIC REAGENTS FOR BORON

1.3.2 Atomic Absorption and Emission Techniques

The use of atomic absorption spectroscopy might be expected to offer a more convenient and interference free method of analysis avoiding the lengthy sample preparation required when using colorimetric techniques. Unfortunately boric oxide formed in the flame has a high dissociation energy. Consequently the limit of detection for boron by atomic absorption spectroscopy is too high for a direct determination (about $4mgl^{-1}$) and it is necessary to use an extraction procedure to enhance the sensitivity. A method has been developed in which boron was extracted from steel solutions in dilute acid into an organic solvent containing 2-ethyl-hexan-1,3-diol (21). Although a rapid procedure, the gain in sensitivity over colorimetric procedures was not sufficient (limit of detection $0.6mgl^{-1}$).

Flame emission spectrophotometry of the organic extract using a nitrous oxide-hydrogen flame gives greater sensitivity (limit of detection $0.05mgl^{-1}$) (22) but spectral interference at the boric oxide molecular band maxima occurs from coextracted cations (23).

Emission from a heated cavity (MECA - molecular emission cavity analysis) containing the dried organic extract gave a similar sensitivity (24).

Recently inductively coupled plasma has been developed for the analysis of elements in solution by atomic emission spectroscopy. Detection limits as low as $0.2\mu gl^{-1}$ for aqueous boron solutions have been recorded using an argon ICP (25) but Lee (26) obtained a detection limit of $0.02mgl^{-1}$ with

brass samples and noted spectral interference from copper and iron. The high cost of ICP instruments (from £50 to 100,K) precludes the general adoption of the technique for elements in solution in the steel industry where it would be unlikely to surplant vacuum emission spectroscopy on solid samples for the control of the production process.

Atomic absorption and emission (and molecular emission) spectroscopy do not appear to provide an overwhelming advantage in terms of sensitivity and/or selectivity over colorimetric procedures for the determination of boron.

1.3.3 Fluorimetric Methods

Fluorimetric procedures are capable of greater sensitivity than colorimetric procedures as the emitted fluorescence intensity is dependent on the intensity of the exciting radiation. Several fluorimetric methods have been employed for some years for the determination of boron in natural waters, effluents and similar samples but have not been followed up by the metallurgical industries.

The reaction of the borate ion with benzoin (Figure 1.10) has been applied to the fluorimetric determination of boron down to 0.005mgl^{-1} in an alkaline ethanolic medium (27,28) Parker and Barnes (29) used the reagent to determine boron in steel (concentration of 0.005%) but employed initial separation of borate by vacuum distillation of the methyl ester and deoxygenation of the fluorescent solution.

Dyes of the rhodamine group (Figure 1.10) when combined as ternary boron complexes with fluoride (30) or salicylic acid (31) and extracted into a benzene-acetone medium, provide another sensitive fluorimetric procedure (limit of detection 0.001mgl^{-1}).

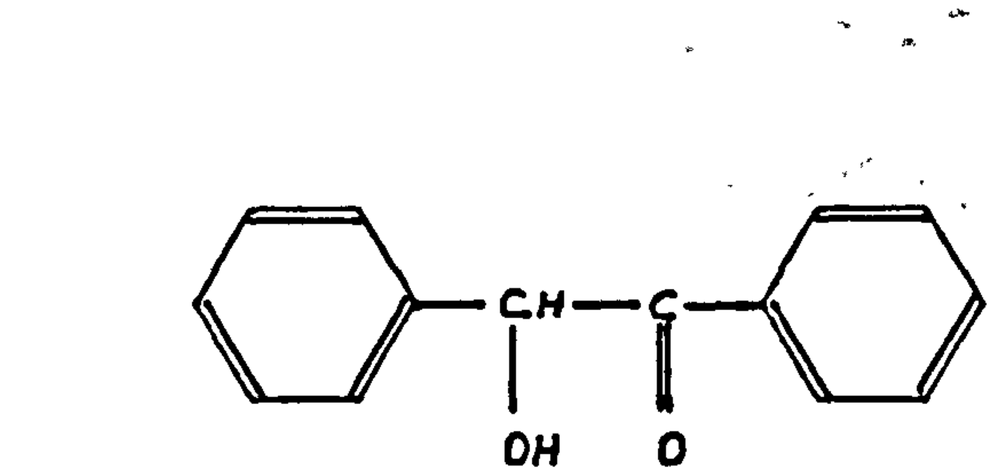
Morin (Figure 1.10) gives a fluorescence with boron when reacted together with oxalic acid, evaporated and extracted into an acetone - ether medium. A limit of detection of 0.0004mgl^{-1} was reported (32).

In neutral aqueous media fluorescence has been used for the determination of boron by Nazarenko et al (33) who investigated sixteen trihydroxyfluorones and obtained 'sensitivity' of 10mgl^{-1} using phenylfluorone. (Figure 1.11)

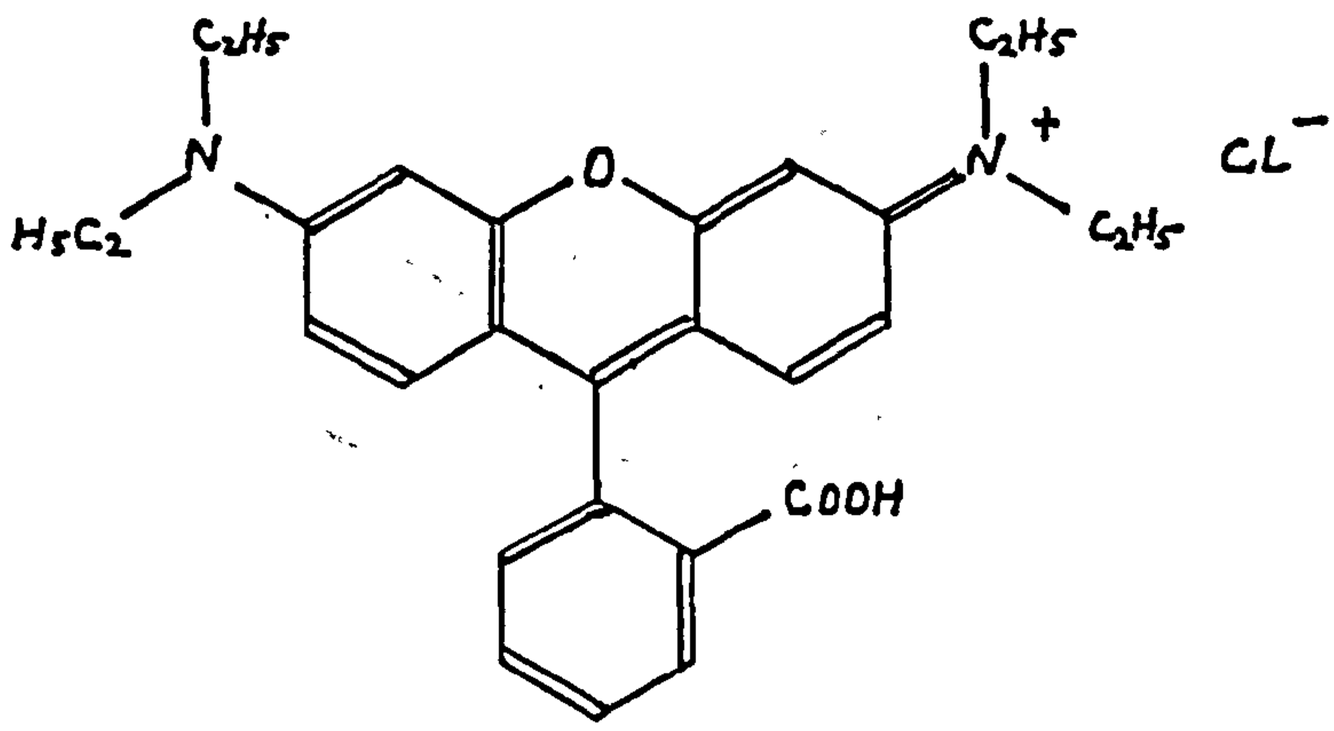
Carminic acid was proposed as a fluorimetric reagent for boron by Bruce and Ashley (34). Fluorescence was developed in phosphate buffer at pH7 but iron interfered and required removal. Gabriels (35) used carminic acid to determine boron in plants, soils and water (limit of detection 0.002mgl^{-1}). Protocatechuic acid (3,4-dihydroxybenzoic acid) has been used for the determination of boron in sea water at pH9. Interferences needed to be separated using chromatography before developing the fluorescence (36). (limit of detection 0.04mgl^{-1}).

Chromotropic acid also fluoresces in neutral solution in the presence of borate. Only a two-fold excess of iron can be tolerated and the reagent is best applied to evaporated methyl borate distillates (37).

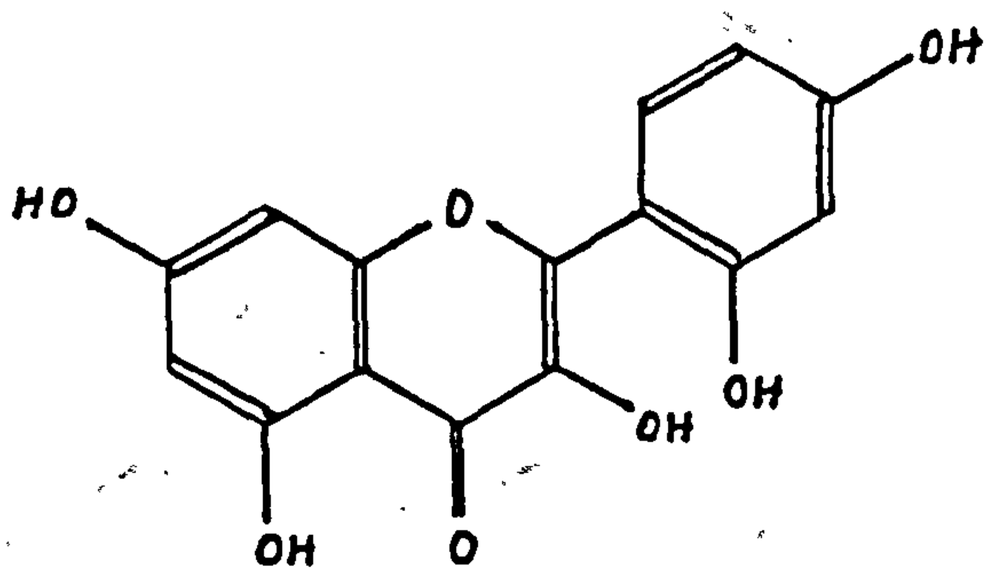
The ideal method for the determination of boron in steel



BENZOIN

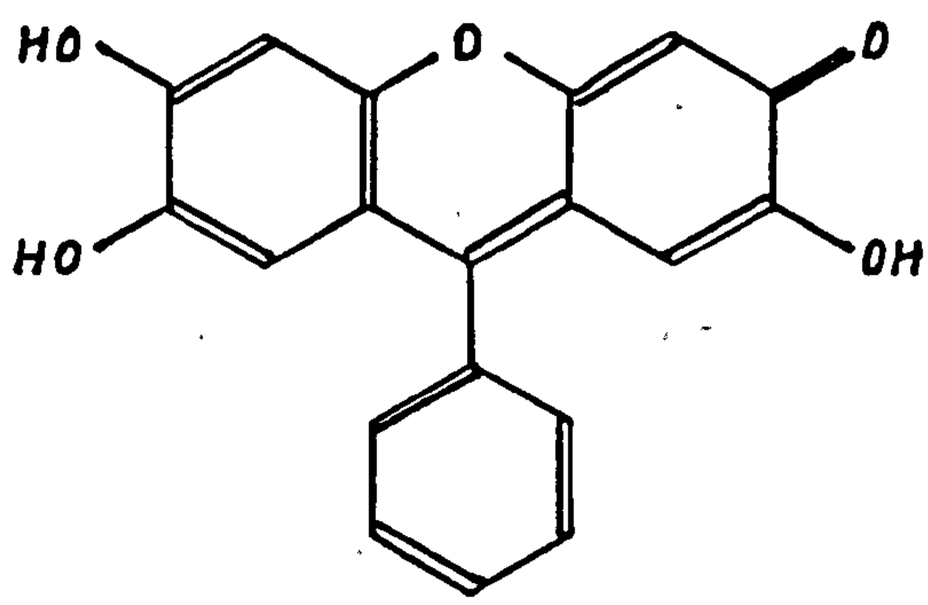


RHODAMINE B

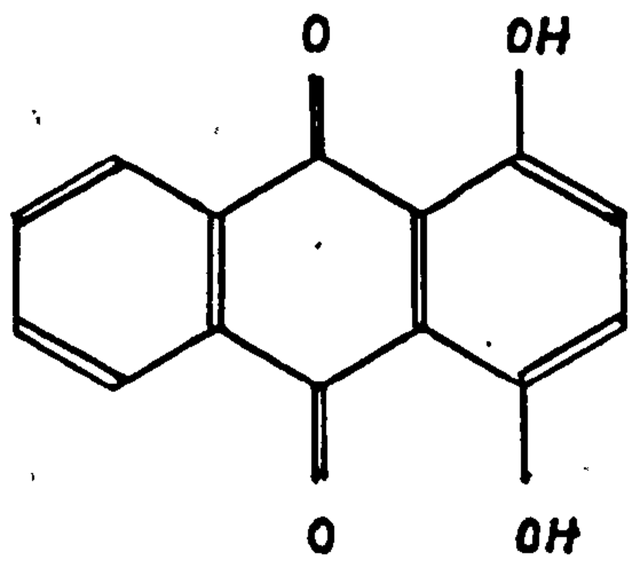


MORIN

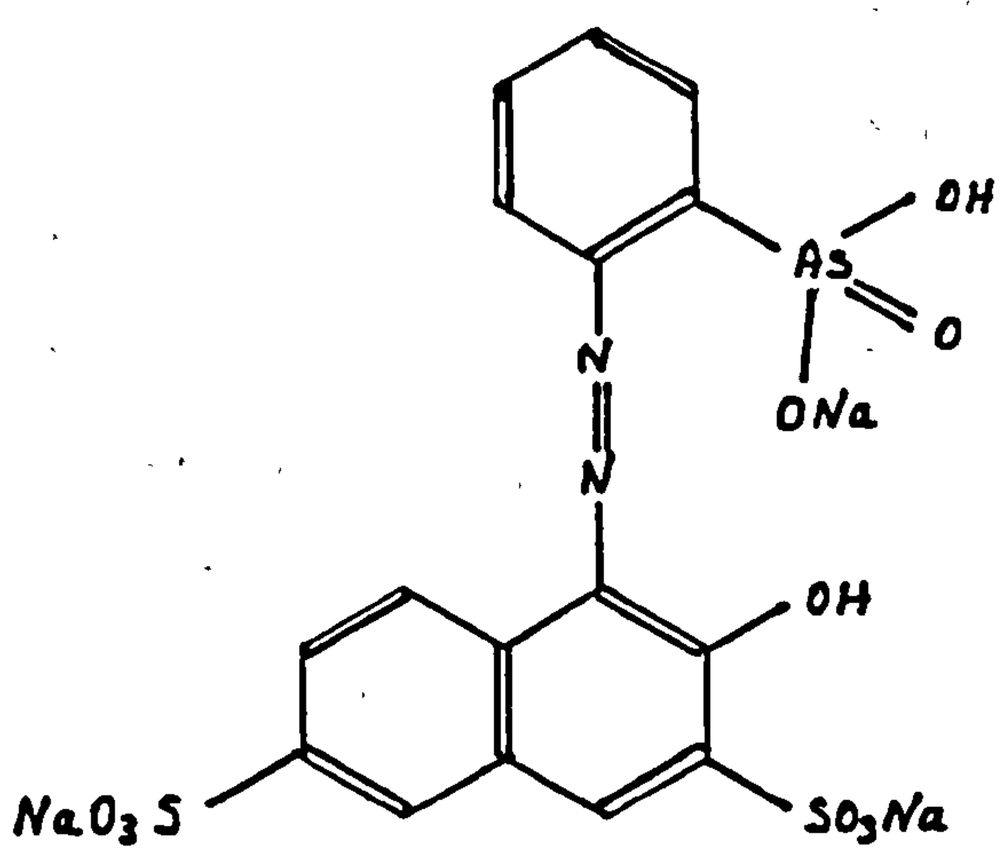
FIGURE 1.10 REAGENTS FOR FLUORIMETRIC DETERMINATION IN ORGANIC MEDIA



PHENYLFLUORONE



QUINIZARIN



THORON

FIGURE 1.11 REAGENTS FOR FLUORIMETRIC DETERMINATION-AQUEOUS AND ACIDIC MEDIA

would be carried out in an acidic medium and require no sample manipulation other than a quantitative dissolution. None of the fluorimetric reagents reviewed above appear to be suitable for use without prior isolation of boron from the iron matrix - the major constraint encountered also in choosing colorimetric procedures. A body of work exists however in which fluorescence with boron is developed in strongly acidic media, and the application of such procedures to the analysis of steels may offer a gain in sensitivity over colorimetric procedures making an attractive alternative to established methods.

Resacetophenone (2',4'-dihydroxyacetophenone) in concentrated sulphuric or syrupy phosphoric acid as solvents has been reported to rapidly produce a fluorescence with boron (38) (limit of detection 1μg). 2,4-Dihydroxybenzophenone is a more sensitive reagent. Monnier, Marcantonatos and Marcantonatos (39) obtained a limit of detection of 0.004mgl^{-1} in 90% sulphuric acid after heating at 70°C for 40 min. Of many metals investigated only vanadium gave interfering fluorescence when present in milligram amounts. The determination of boron (2 to 10mgl^{-1}) in copper and nickel has been described using this reagent (40). Marcantonatos and co-workers went on to study more substituted 2-hydroxybenzophenones which gave fluorescence with boron and proposed HMCB (2-hydroxy-4-methoxy-4'-chlorobenzophenone) as the most sensitive (limit of detection 0.0004mgl^{-1}). This reagent however also required heating at 70°C for development of maximum fluorescence; at ambient temperature this was not achieved before partial oxidation of reagent occurred (41). Nevertheless HMCB has been applied to the direct determination

of boron in many matrices - sodium hydroxide (42), steel (43), plants (44), water (45), blood (46).

An automated procedure using this reagent has been described for the determination of the different chemical forms of boron normally present in water (47) (limit of detection 0.001mgl^{-1}).

Traces of boron (.005mgl^{-1}) have been determined by a 'luminescent' procedure using dibenzoylmethane (48) in concentrated sulphuric acid - ethyl ether medium and applied to the fluorimetric determination of boron in high purity aluminium (49).

Other reagents which have been used for the fluorimetric determination of boron in strong sulphuric acid are quinizarin (50) and thoron (51) (Figure 1.11). The latter develops maximum fluorescence in an hour at ambient temperature in 90% sulphuric acid and has been used for the determination of boron in silicon tetrachloride (52) (limit of detection 0.002mgl^{-1}).

This last group of reagents which form fluorescent complexes with boron in strong sulphuric acid offer similar sensitivity to reagents which fluoresce in neutral media and may be applicable to the analysis of steel. It is desirable that the fluorescence should be unaffected by an excess of iron and be rapidly developed without the need for heating to promote complex formation. As steel cannot be readily dissolved in sulphuric acid more concentrated than 20 - 30% the reagent should be sufficiently sensitive to take account of the reduced boron content which can be introduced into a 90 - 95% sulphuric acid fluorescent solution.

The study of the reagents which most closely meet these requirements forms the basis of the experimental portion of this work.

2. INVESTIGATION OF COMPOUNDS FORMING FLUORESCENT COMPLEXES WITH BORON AND THEIR APPLICATION TO THE ANALYSIS OF STEEL

The introductory chapter has illustrated the need to determine trace amounts of boron in steel solutions. Existing atomic spectroscopic techniques which are widely applied to the determination of trace constituents in steels are not ideal for the determination of boron due to lack of sensitivity. Atomic emission - ICP, whilst providing sufficient sensitivity, requires separation of boron from the iron matrix to achieve the desired reproducibility and freedom from interference. Colorimetric procedures can provide the requisite sensitivity and have been widely investigated; usually some means of separation is employed. The group of compounds which fluoresce in strongly acidic media, however, appear to offer the opportunity for a direct determination of the small amounts of boron commonly found in steels.

2.1 Instrumental considerations

Fluorescence spectroscopy offers intrinsic high sensitivity and high selectivity.

The molecular processes involved in fluorescence result in the wavelength of the emitted fluorescent radiation being greater than that of the absorbed exciting radiation. The fluorescence signal received by the spectrophotometer detector is thus measured superimposed on a small background signal in contrast to a small difference in two large signals with absorption spectrophotometry.

The fluorescence intensity, I_f, is dependent on the intensity of the exciting radiation, I_o, according to the relationship

$$I_f = K\phi_f I_o(1 - 10^{-\varepsilon cl})$$

which for low concentrations, (εcl less than 0.01), reduces to

$$I_f = 2.3K\phi_f I_o \varepsilon cl$$

where K is a constant depending on geometric factors, ϕ_f is the fluorescence quantum efficiency, ε the molar absorptivity, c the concentration of fluorescing species and l the absorbing path length.

This can be further simplified to

$$I_f = \phi I_o \varepsilon cl$$

if ϕ is defined as the apparent fluorescence efficiency.

An intense radiation source will give a corresponding strong fluorescence - providing that photodecomposition of the irradiated solution does not occur. Two fluorescent complexes excited at the same wavelength may fluoresce at differing wavelengths, and the reverse may also occur. A selective determination may be made by the appropriate choice of excitation and emission wavelengths.

In the simplest type of fluorimeter both exciting and emitted radiation are selected by optical filters. With filter-monochromator instruments excitation radiation is selected by filter and emitted radiation passes through a monochromator to the photodetector. The emission spectrum can thus be recorded over a range of wavelengths. If a line source such as a mercury arc

is used essentially monochomatic excitation radiation can be achieved with both these instruments. In dual monochromator instruments both excitation and emitted radiation pass through monochromators. By keeping either excitation or emission wavelengths constant and varying the other an emission or excitation spectrum can be obtained. The Perkin Elmer - Hitachi - MPF 2A spectrofluorimeter used in this work for all fluorescence measurements is of this type. It has fully adjustable slits, and a 125 watt xenon arc light source. Measurements were made using a ratio mode in which a small fraction of the exciting radiation is directed to a reference photomultiplier, the output of which is used to control the voltage to the sample photomultiplier tube so that although any instability of the source produces a change in output of both detectors, their ratio remains unchanged. The instrument uses 90^{o} geometry in which the fluorescent radiation is measured at right angles to the excitation radiation so reducing the intensity of radiation at the excitation wavelength entering the emission monochromator. The sample solution was contained in a 1cm silica cell polished on all four sides.

A Pye Unicam SP 800 recording spectrophotometer was used for absorption measurements.

2.2 Fluorimetric reagents

Reagents forming fluorescent complexes with boric acid in organic or neutral aqueous media require the removal of the iron matrix before they can be applied to the analysis for

boron in steel. Complexes which fluoresce in strong acidic media have the potential for direct determinations. Substituted benzophenones have been widely studied as reagents for the direct determination of boron in a range of matrices and although capable of providing a sensitive direct method they suffer certain limitations, primarily the requirement for heating to provide a rapid development of fluorescence. Other reagents giving fluorescence in acidic media have been less thoroughly investigated and reported work has been confined mainly to pure boric acid solutions.

Resacetophenone and thoron were initially chosen for further study as these reagents had been reported to produce fluorescence with boric acid at ambient temperature in strong but not concentrated sulphuric acid and were readily available.

Some other arsenophenylazonaphthalene derivatives which had not previously been reported to give fluorescence with boric acid were also investigated.

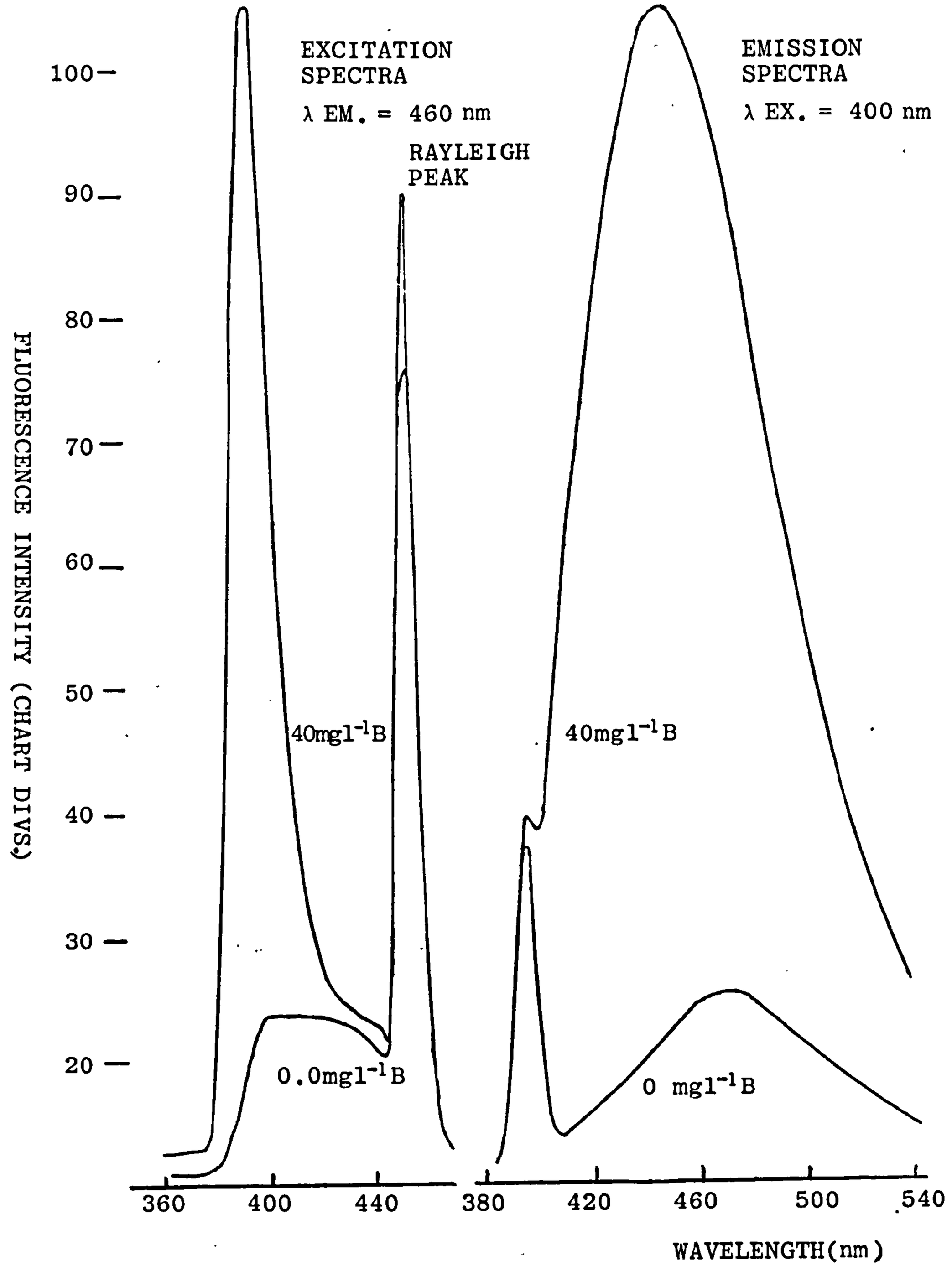
2.2.1 Resacetophenone (2,4-dihydroxyacetophenone)

Gopala Rao et al.(38) found a 0.1% solution of pure resacetophenone in concentrated sulphuric acid gave an immediate blue fluorescence with boric acid in 96% v/v sulphuric acid. They obtained a linear calibration graph over the range 40 to 400mgl^{-1} boric acid. Neelakantam et al.(53) had previously found the fluorescence to be unaffected by the coloured ions Ni^{2+}, Co^{2+} and Cr^{3+} at 'medium' concentrations and that fluorescence occurred also in syrupy phosphoric acid.

Initial investigation using the conditions proposed by Gopala Rao showed a single broad band of fluorescence with a maximum intensity at 460 nm. (Figure 2.1). The excitation spectra showed maximum fluorescence from the complex at 400 nm but the reagent gave a broad band of fluorescence (excitation maximum 420 nm) which overlapped the boron excitation spectra. Recrystallizing the reagent several times from water containing a little hydrochloric acid gave nearly colourless crystals and eliminated most of this background fluorescence enabling the fluorescence from more dilute boric acid solutions to be measured. Residual fluorescence from the reagent, or impurities that remained, still, however, limited the usable sensitivity. At the levels of boron encountered in steel the fluorescence from the blank, boron free, solution was many times greater than that due to boron (Figure 2.2). The limit of detection obtained was about 0.05mgl^{-1} boron in the measured solution. If the initial steel solution was 1%w/v in 30% v/v sulphuric acid (the maximum concentration which can be conveniently prepared) this is equivalent to 0.01% boron content.

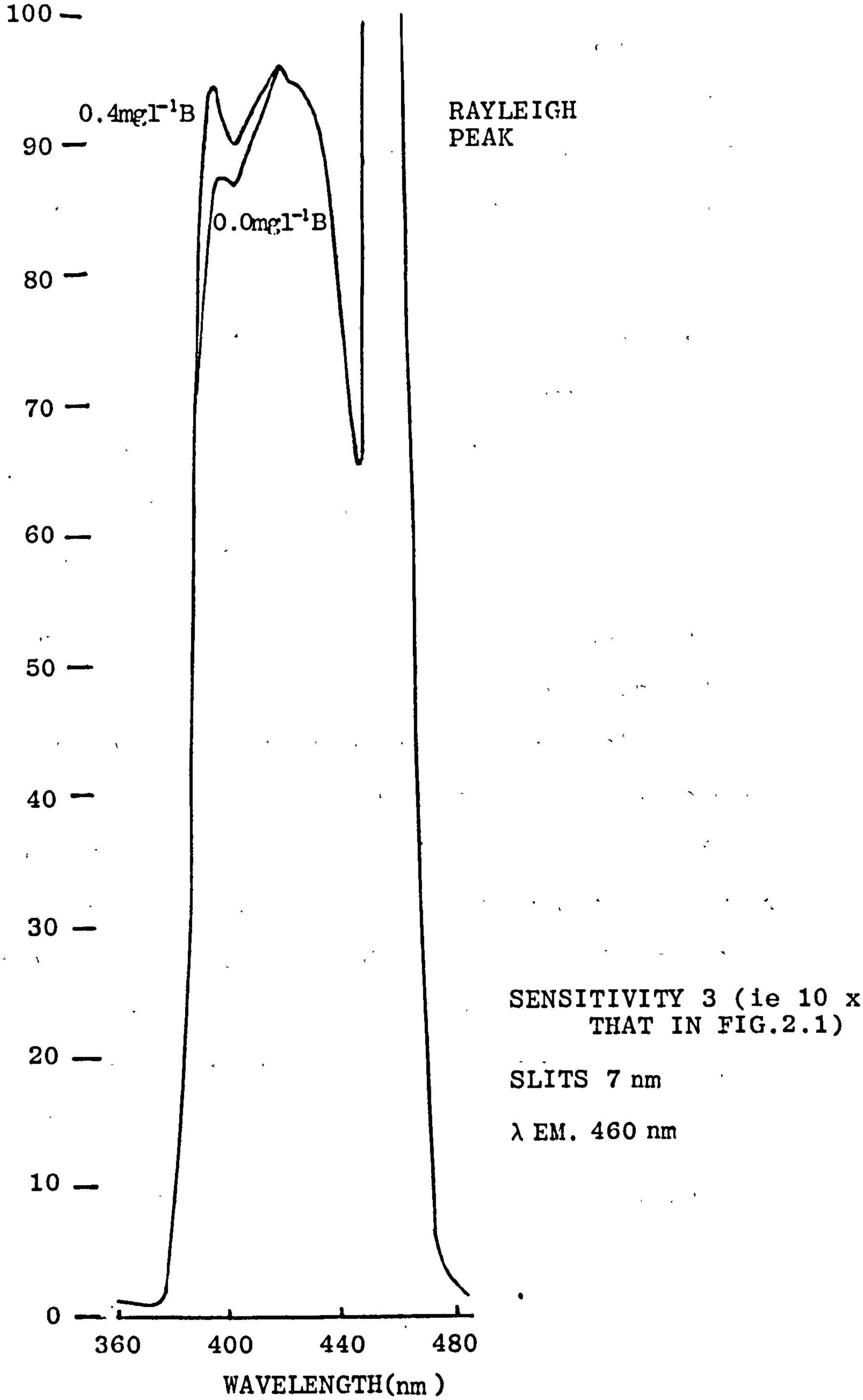
The inability to completely suppress the unwanted fluorescence using the fluorimeter back-off control limited the use of increased fluorimeter gain. It is probable the fluorescence arising from the reagent could be reduced by further purification, but it is likely that the sensitivity would still be limited by the level of background fluorescence which would have to be reduced by a factor of ten or more before this reagent could be considered satisfactory for the desired application.

FIGURE 2.1 FLUORESCENCE SPECTRA
2,4-DIHYDROXYACETOPHENONE-BORIC ACID COMPLEX



SENSITIVITY 1 SLITS 7 nm

FIGURE 2.2 EXCITATION SPECTRA 2,4-DIHYDROXYACTOPHENONE BORIC ACID COMPLEX NEAR LIMIT OF DETECTION



2.2.2 Thoron

The reagent 1-(2′-arsenophenylazo)-2-hydroxynaphthalene-3, 6-disulphonic acid was first introduced by Kuznetsov in 1941 for the detection of thorium. It is known by various trivial names:- thoron, thorin, thoronol, naptharson, and apans. The reagent is commercially available in the form of its trisodium salt under the name of thoron.

Marcantonatos et al (51) first reported fluorescence from a boric acid - thoron complex formed in concentrated or 'a little diluted' sulphuric acid. They proposed a procedure which was 'a little less sensitive than using benzoin but which did not require special precautions'.

Maximum fluorescence was obtained at 587 nm using excitation radiation from a mercury lamp at 390 nm. In concentrated sulphuric acid maximum fluorescence was obtained only after 30 hours at room temperature but at 90°C the time was reduced to 60 minutes. In the presence of 8 to 16% water the time for development of fluorescence, at ambient temperature, was greatly reduced, the maximum being obtained in about one hour. An excess of thoron over boric acid was required for maximum fluorescence; similar results were obtained with two to four fold molar excess.

From these observations they proposed the following procedure:

To 2ml of solution containing 10-16% of water in sulphuric acid and 0.03 to 2.1µg boron

Add 0.8ml of concentrated sulphuric acid

0.2ml of thoron (0.13% in concentrated sulphuric acid)

Mix and stand for 90 minutes.

Measure fluorescence at 587 nm against a blank solution when the excitation wavelength is about 365 nm.

A straight line calibration graph was obtained using this procedure over the range 0.007 to 0.07mgl^{-1} boron in the measured solution. This would correspond to approximately 0.005 to 0.05% boron in an initial 1% steel solution in 30% sulphuric acid.

The work of Marcantonatos et al thus appears to offer the basis of a simple rapid and sensitive method for the determination of boron in steel.

The fluorescence was reinvestigated using the MPF 2A dual monochromator fluorimeter. Using the method proposed by Marcantonatos et al as a basis, a fluorescent solution containing 0.015mgl^{-1} boron was prepared and excitation and emission spectra were recorded. Two broad coalesced bands of similar intensity were evident in the excitation spectrum with maxima at 420 and 476 nm. The fluorescence emission was a single peak reaching a maximum at 580 nm. (Figure 2.3). Figure 2.4 shows the corresponding absorption spectrum of the fluorescence solution.

A series of solutions was prepared as follows:

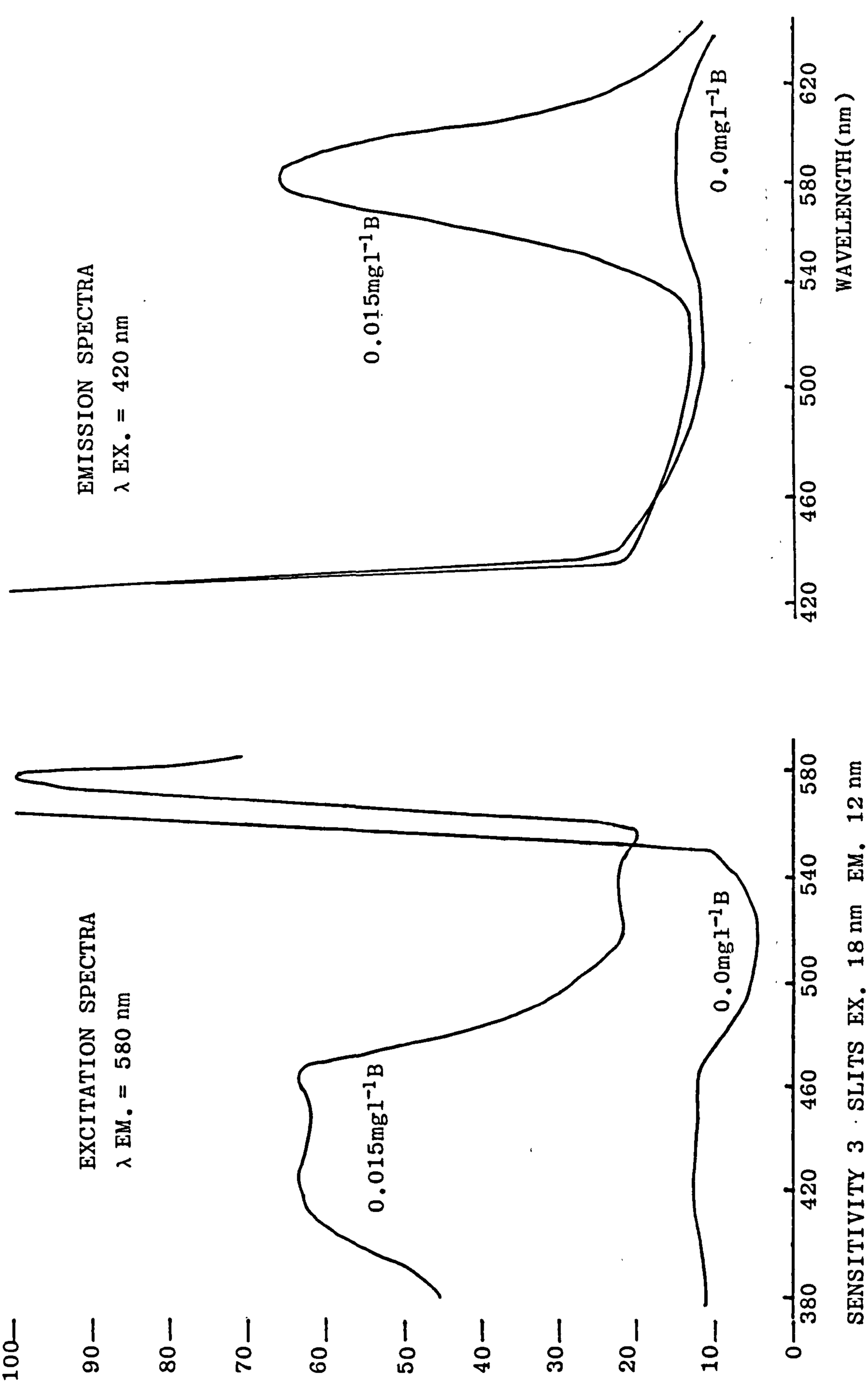


FIGURE 2.3 FLUORESCENCE SPECTRA THORON-BORIC ACID COMPLEX

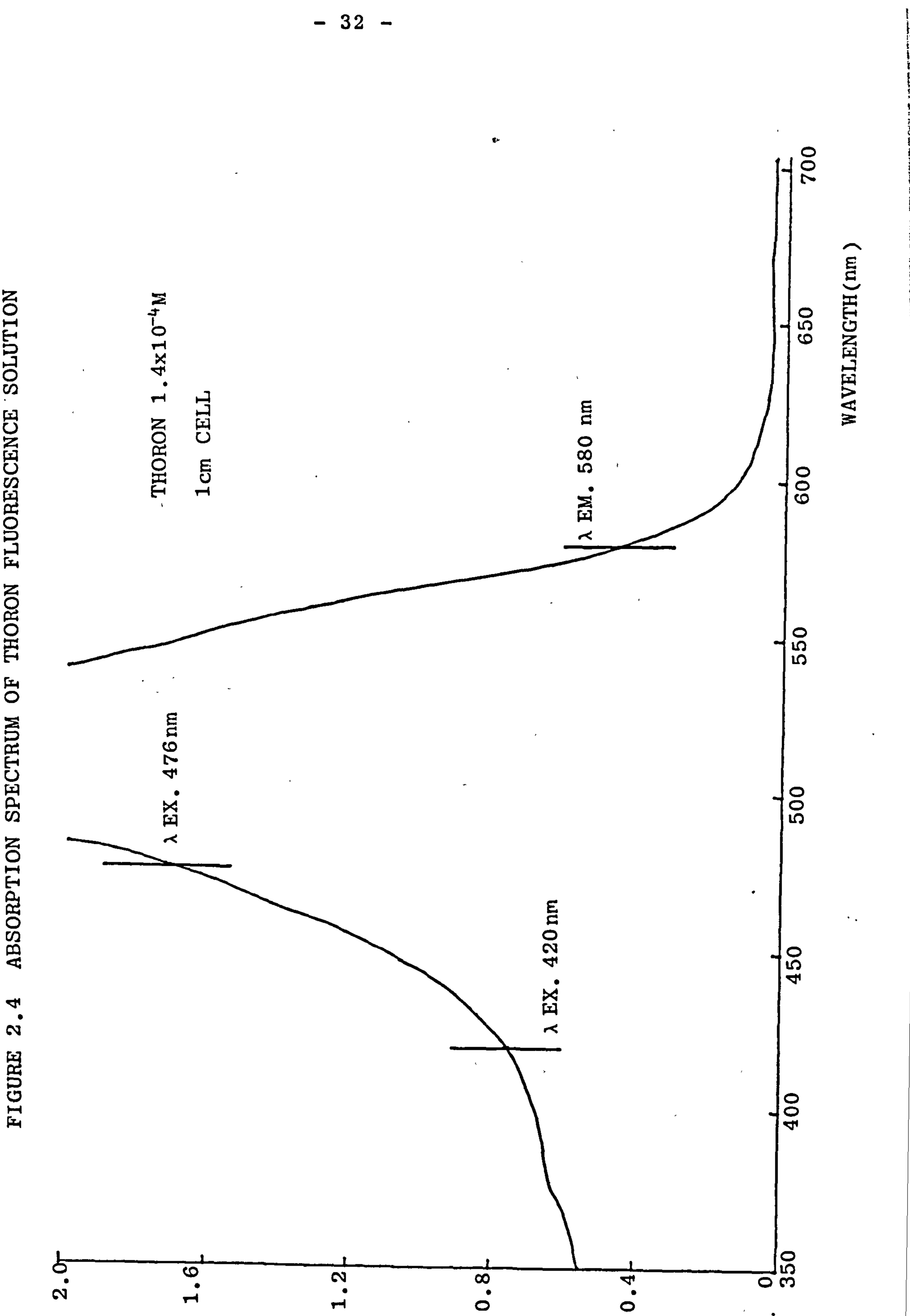


FIGURE 2.4 ABSORPTION SPECTRUM OF THORON FLUORESCENCE SOLUTION

15ml solution of known amount of boric acid in sulphuric acid (30% v/v).
10ml thoron (0.086%w/v) in concentrated sulphuric acid made up to 100ml with concentrated sulphuric acid, mixed and stood 90 minutes.

giving a final sulphuric acid concentration in the fluorescent solution of approximately 90% v/v. Their fluorescence was measured at 580 nm with excitation at 420 nm. The graph of fluorescence intensity versus concentration was linear up to about 0.5mgl^{-1} boron equivalent to 0.033% boron in a 1% steel solution.(Figure 2.5). This is above the levels encountered in practice. The graph becomes curved at higher concentrations and from 3.5mgl^{-1} upwards the graph becomes linear again but with a reduced slope. Extensions of the linear portions of the graph intersect at 1.6mgl^{-1} boron (approximately 1.5×10^{-4}M boric acid). The thoron concentration of the fluorescent solutions was 1.44×10^{-4}M.

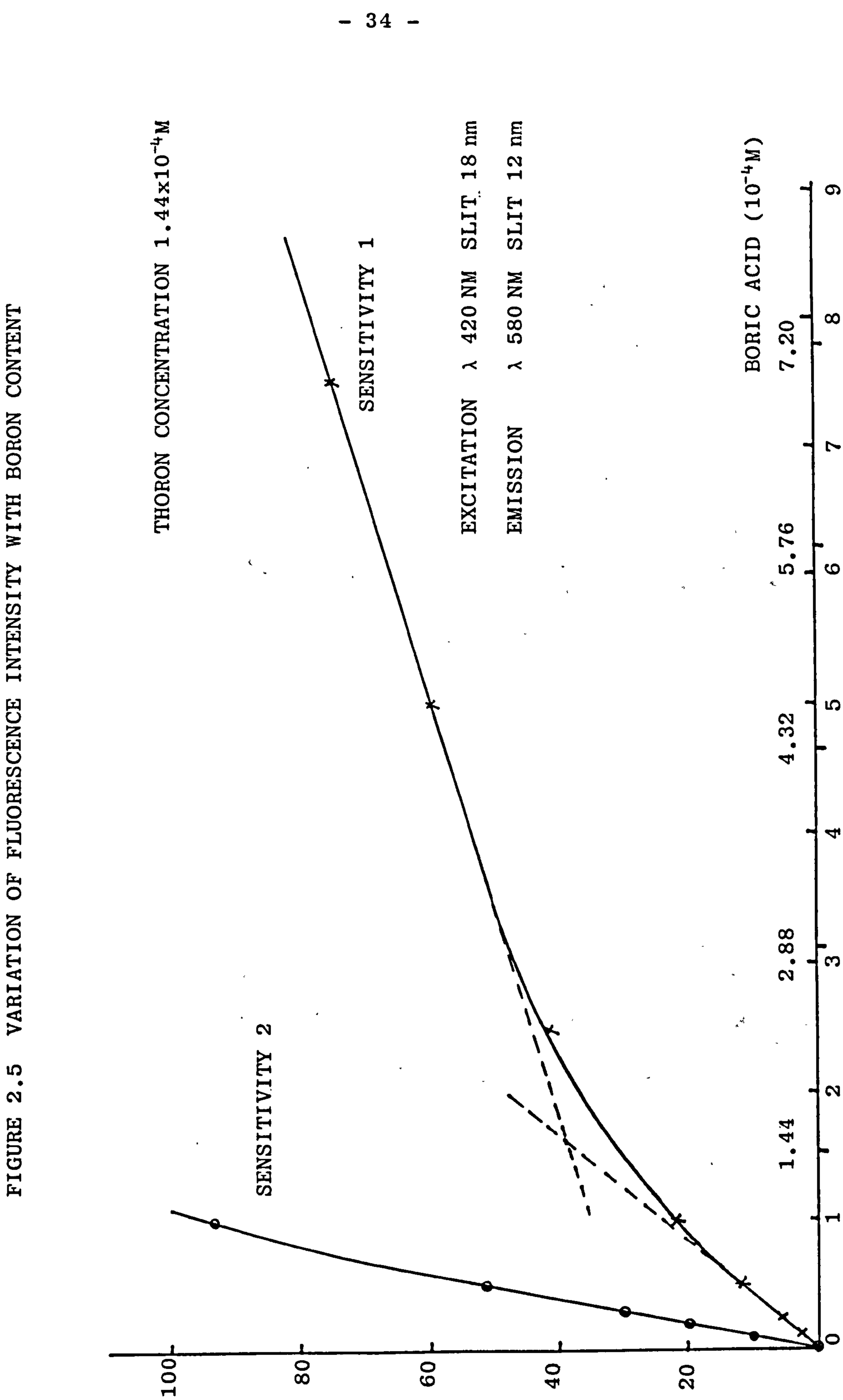
2.2.3 Other arsenophenylazonaphthalene derivatives

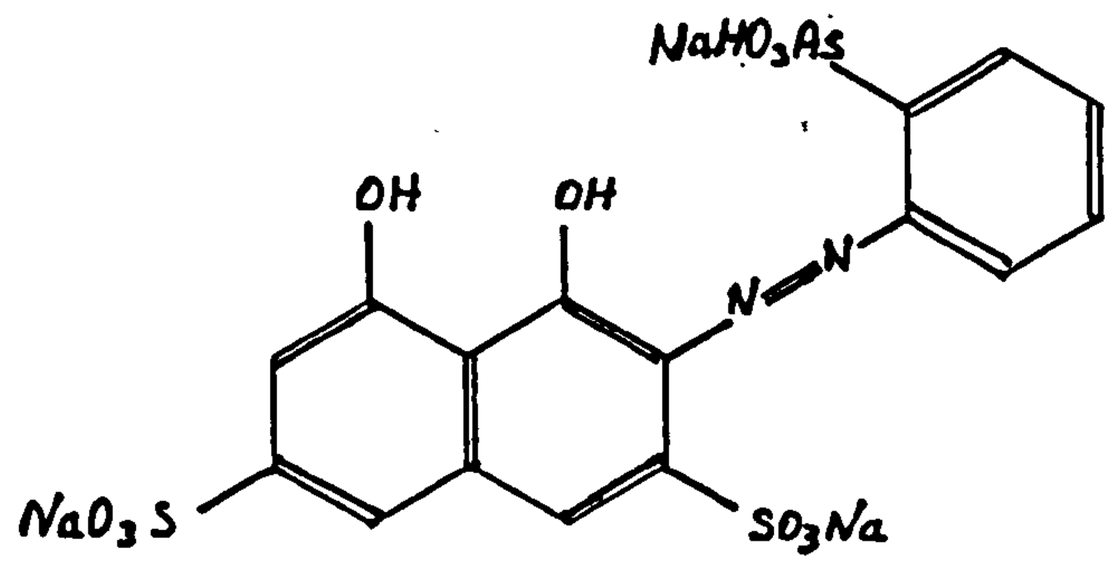
(a) Arsenazo I

This compound (Figure 2.6) has been reported to form a coloured complex with boric acid in sulphuric acid medium (18) but has not previously been investigated as a fluorimetric reagent.

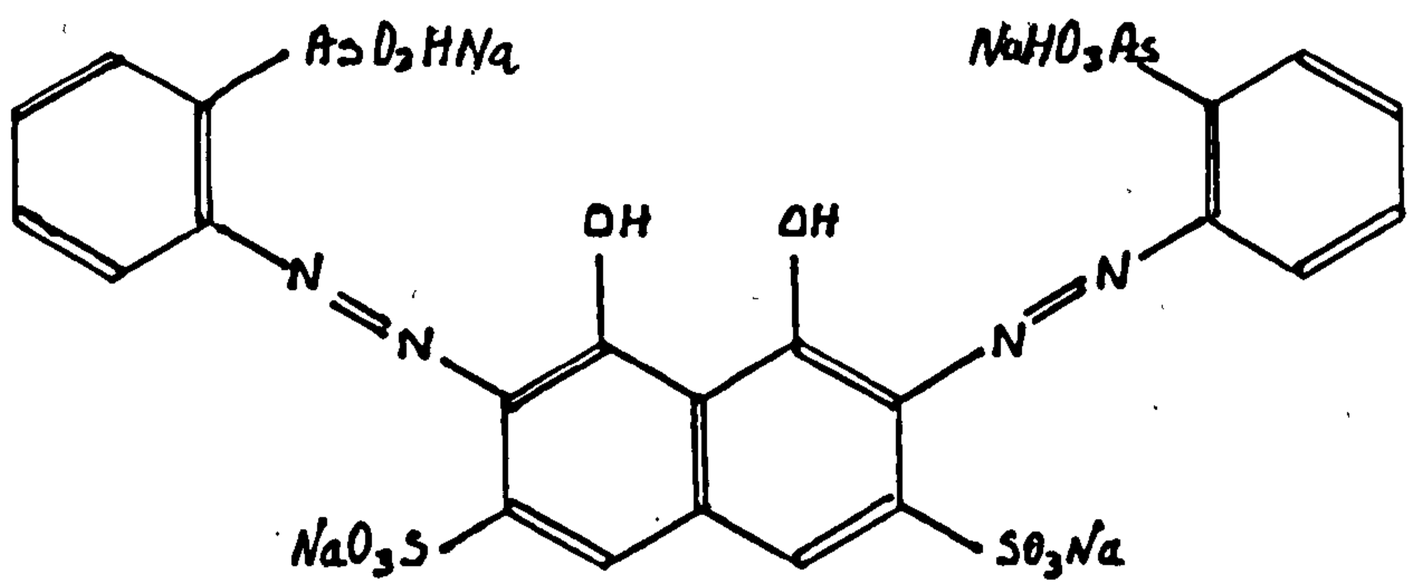
Solutions containing arsenazo I and boric acid were prepared similarly to those used for thoron and were examined for fluorescence from the boric acid complex.

FIGURE 2.5 VARIATION OF FLUORESCENCE INTENSITY WITH BORON CONTENT

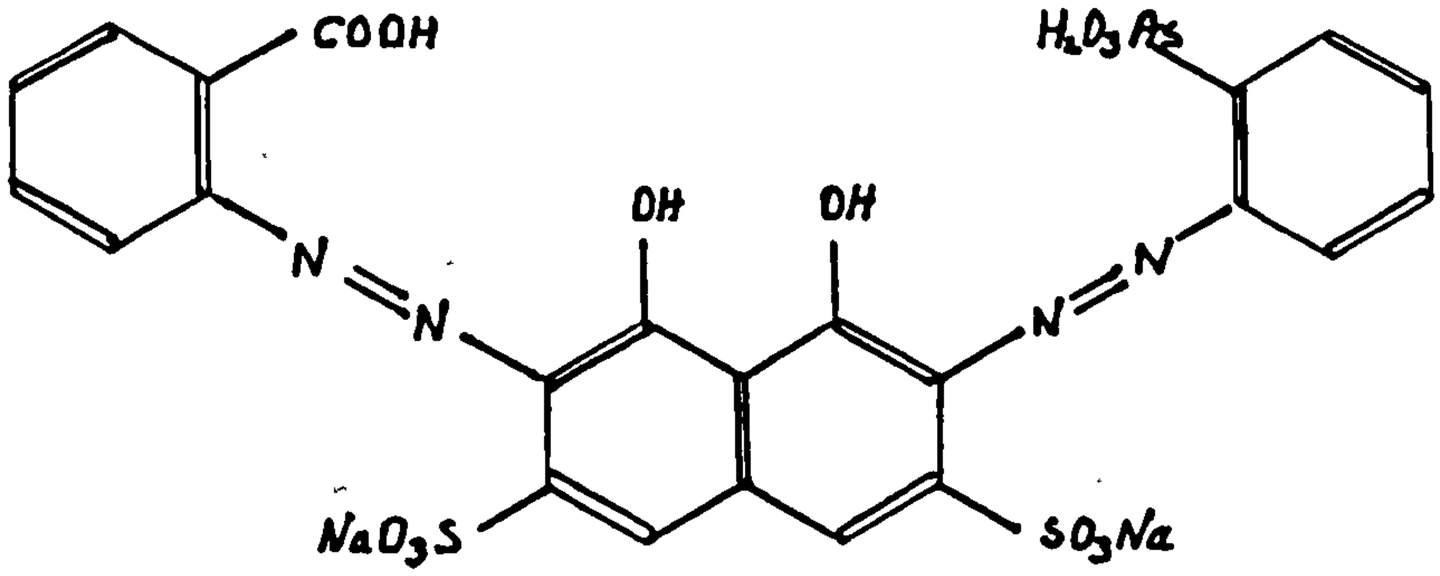




ARSENAZO I



ARSENAZO III



CARBOXYARSENAZO III

FIGURE 2.6 ARSENOPHENYLAZONAPHTHALENE DERIVATIVES

Fluorescence was observed at shorter wavelengths than with thoron (Figures 2.7, 2.8) and the Stokes' shift was much less. The wavelengths of maximum fluorescence were 350 nm for excitation and 380 nm for emission.

(b) Arsenazo III

Arsenazo III has not been reported as forming a complex with boric acid but fluorescence was observed from a 10^{-4}M solution in 90% sulphuric acid containing 1.5mgl^{-1} boron.

Maximum fluorescence occurred at the wavelength of minimum absorption when irradiated with undispersed radiation from the xenon arc.(Figures 2.9, 2.10). Irradiating at specific wavelengths greatly reduced the fluorescence obtained as the reagent solution was intensely coloured and showed little transmission in the visible spectrum.

(c) Carboxyarsenazo III

The solution of this reagent in sulphuric acid is even more intensely coloured than that of arsenazo III. Solutions showing any transmission were of similar concentration to the boron levels being investigated. Fluorescence due to the presence of boron could not be detected from a 10^{-5}M solution, in 90% sulphuric acid, to which excess boric acid had been added (1.5mgl^{-1} boron approximately, 1.5×10^{-4}M boric acid). Figure 2.11 shows the absorption spectrum of this reagent.

Arsenazo I appears to be less suitable than thoron for the fluorimetric determination of boron using a filter fluorimeter

FIGURE 2.7 FLUORESCENCE SPECTRA ARSENAZO I

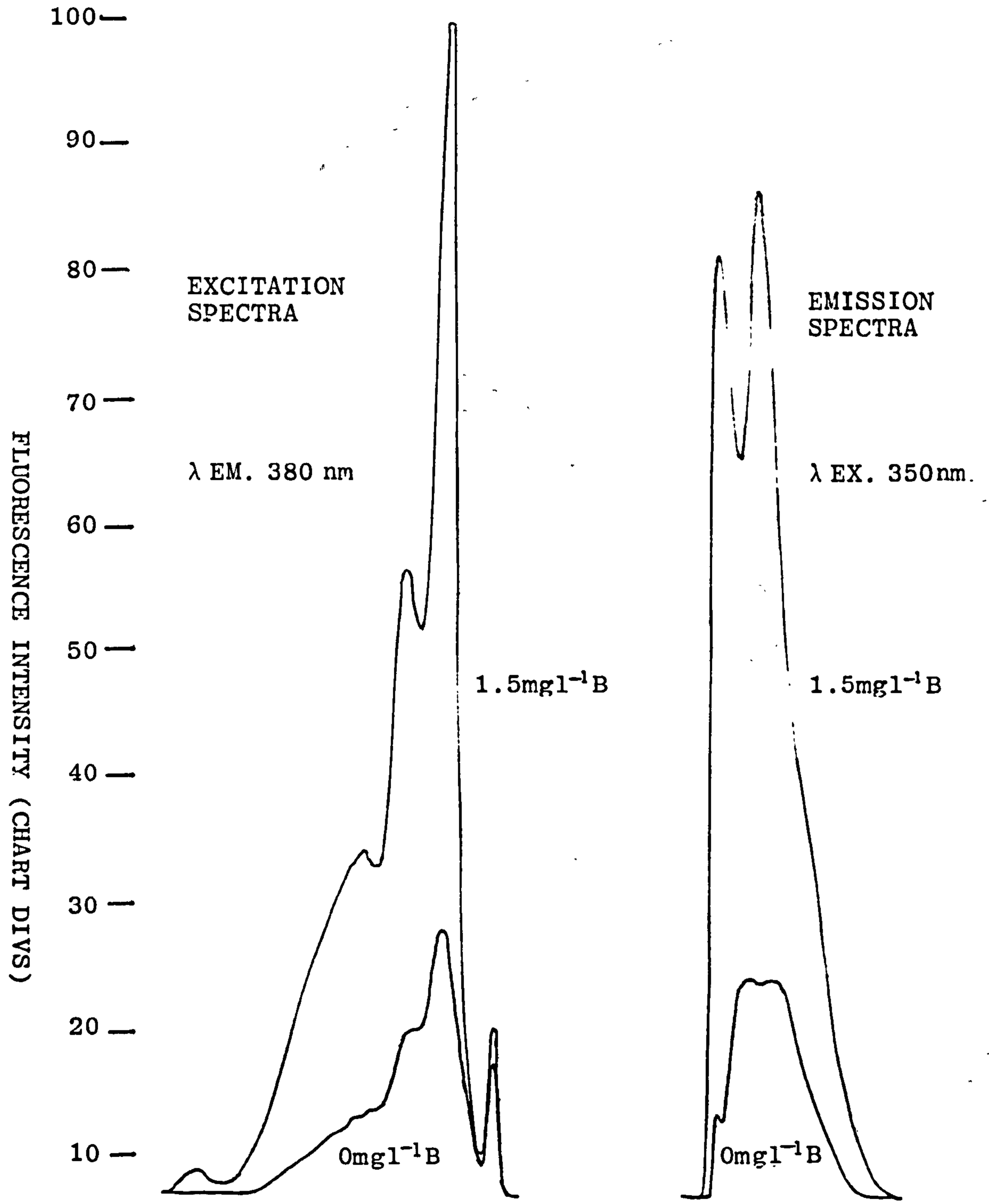


FIGURE 2.8 ABSORPTION SPECTRA ARSENAZO I FLUORESCENCE SOLUTIONS

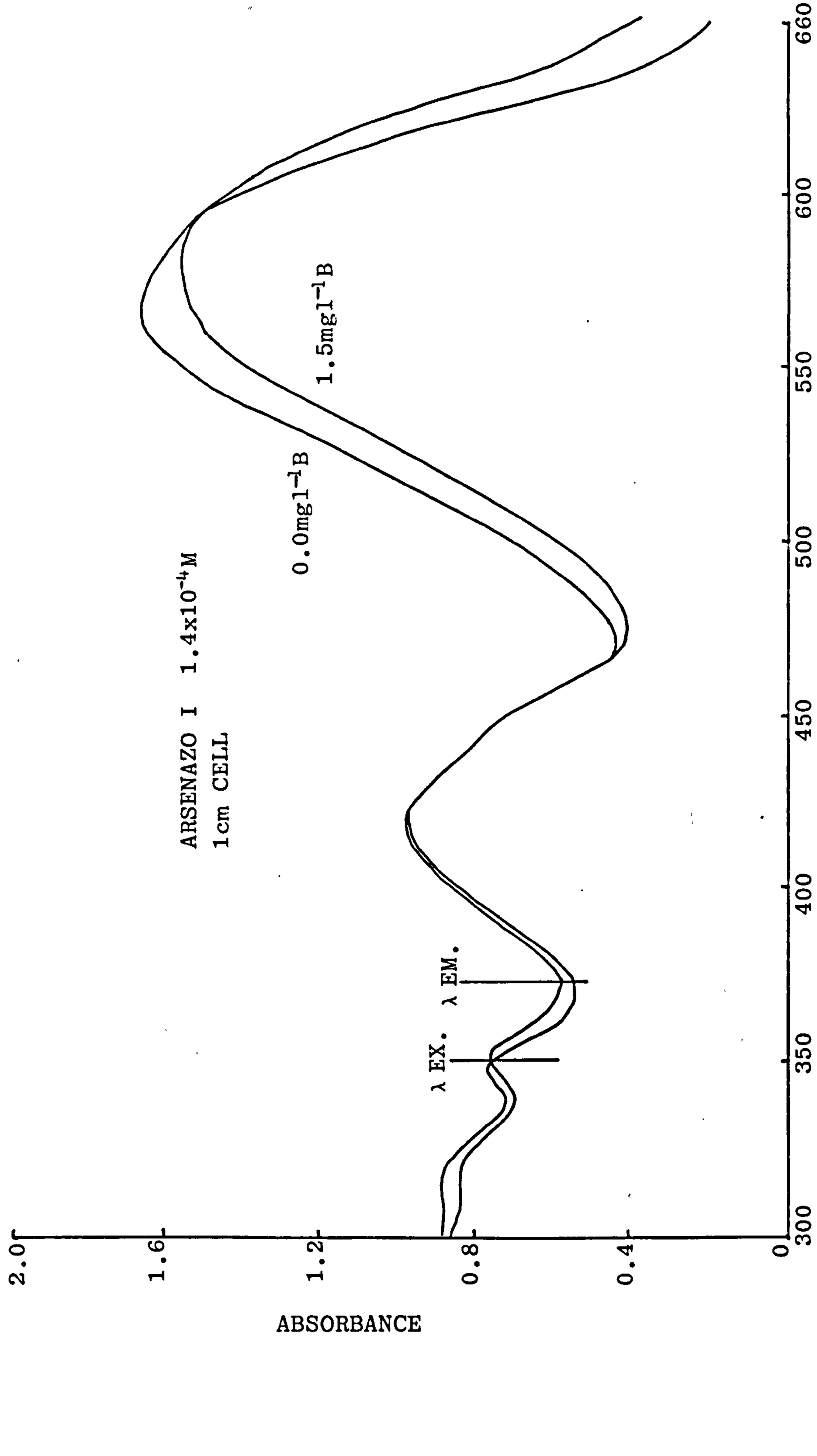
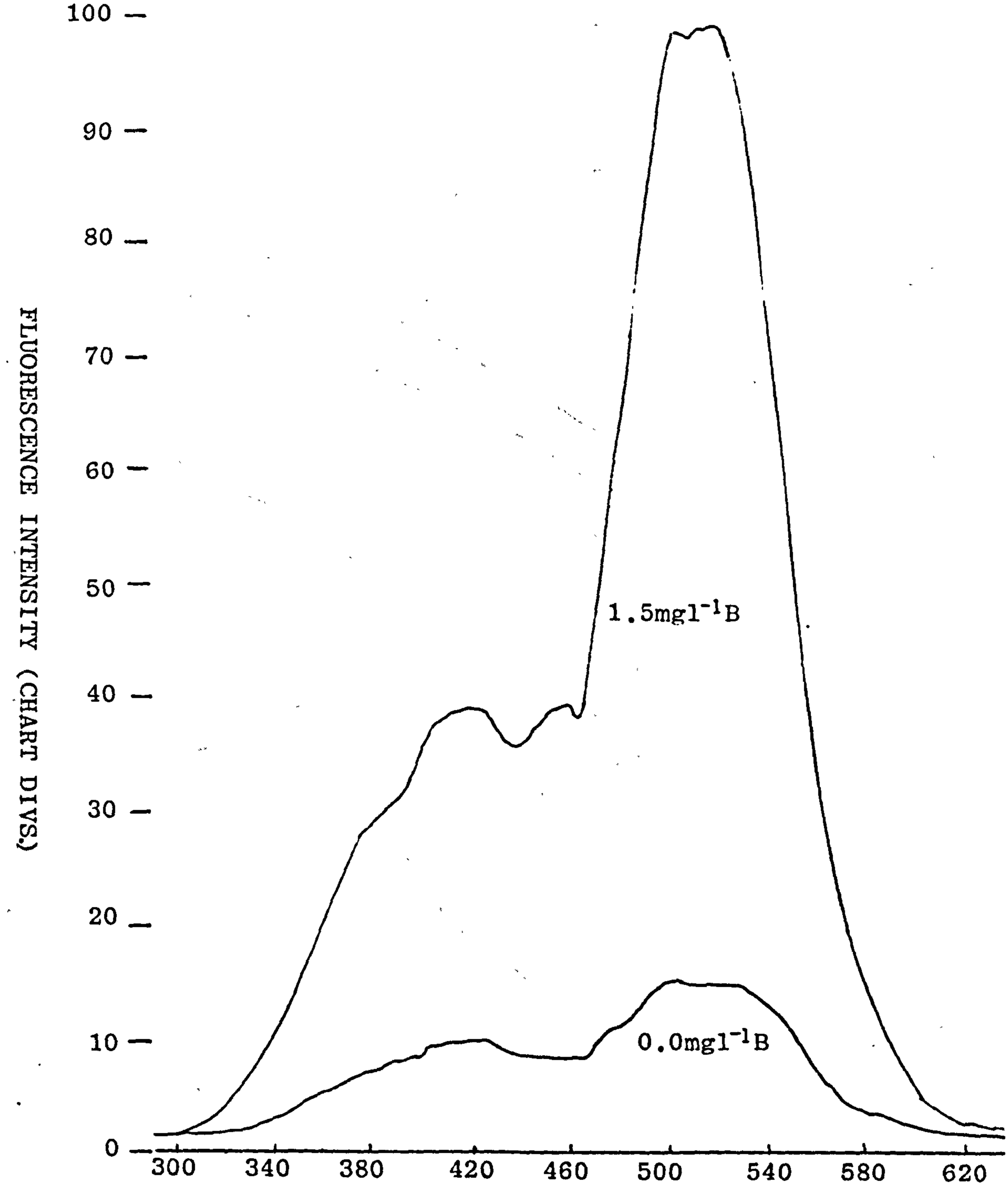


FIGURE 2.9 FLUORESCENCE EMISSION SPECTRA ARSENAZO III BORIC ACID SOLUTIONS



SENSITIVITY 3 SLITS EX. 4 nm EM. 18 nm EXCITATION UNDISPERSED

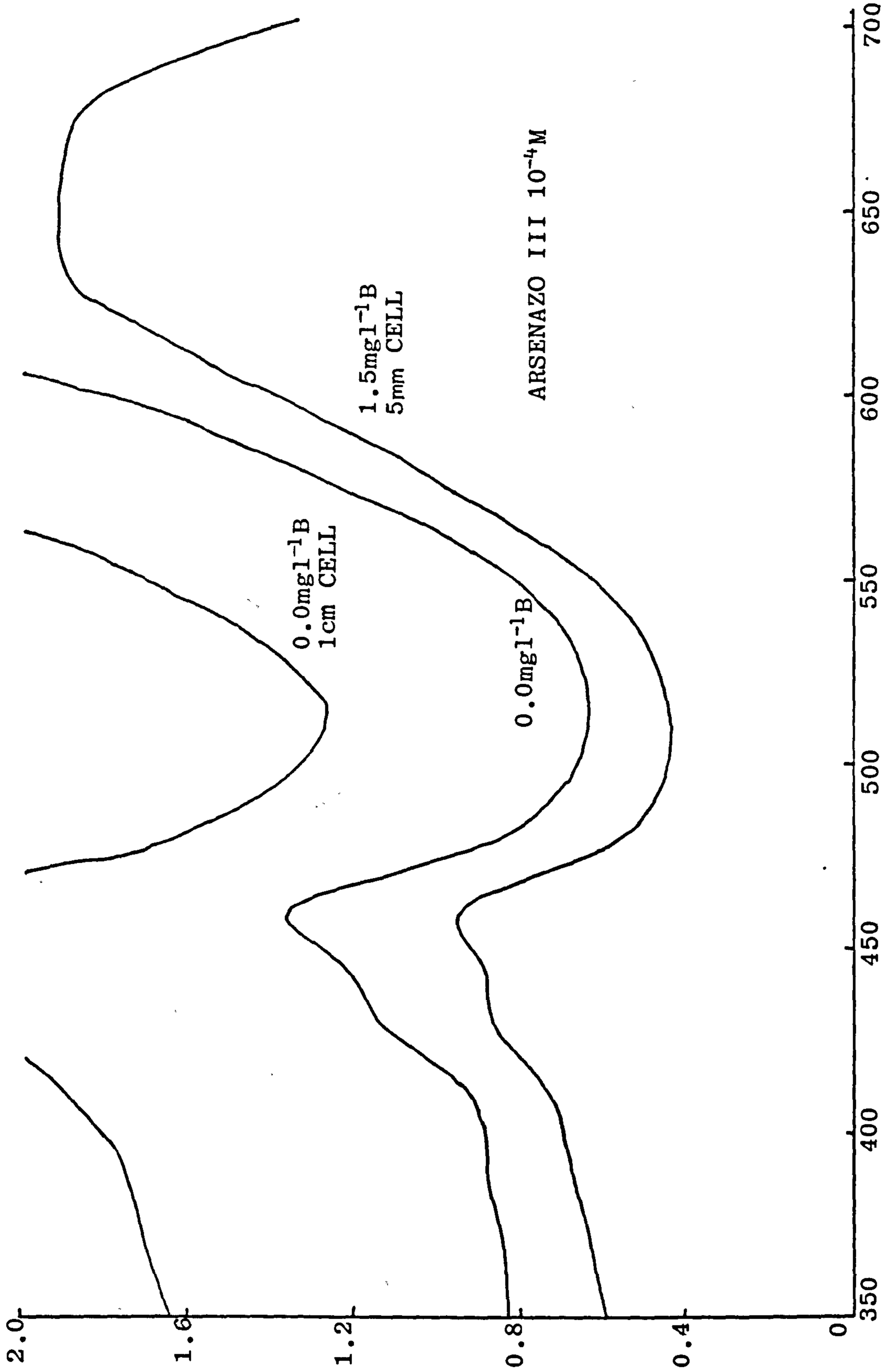
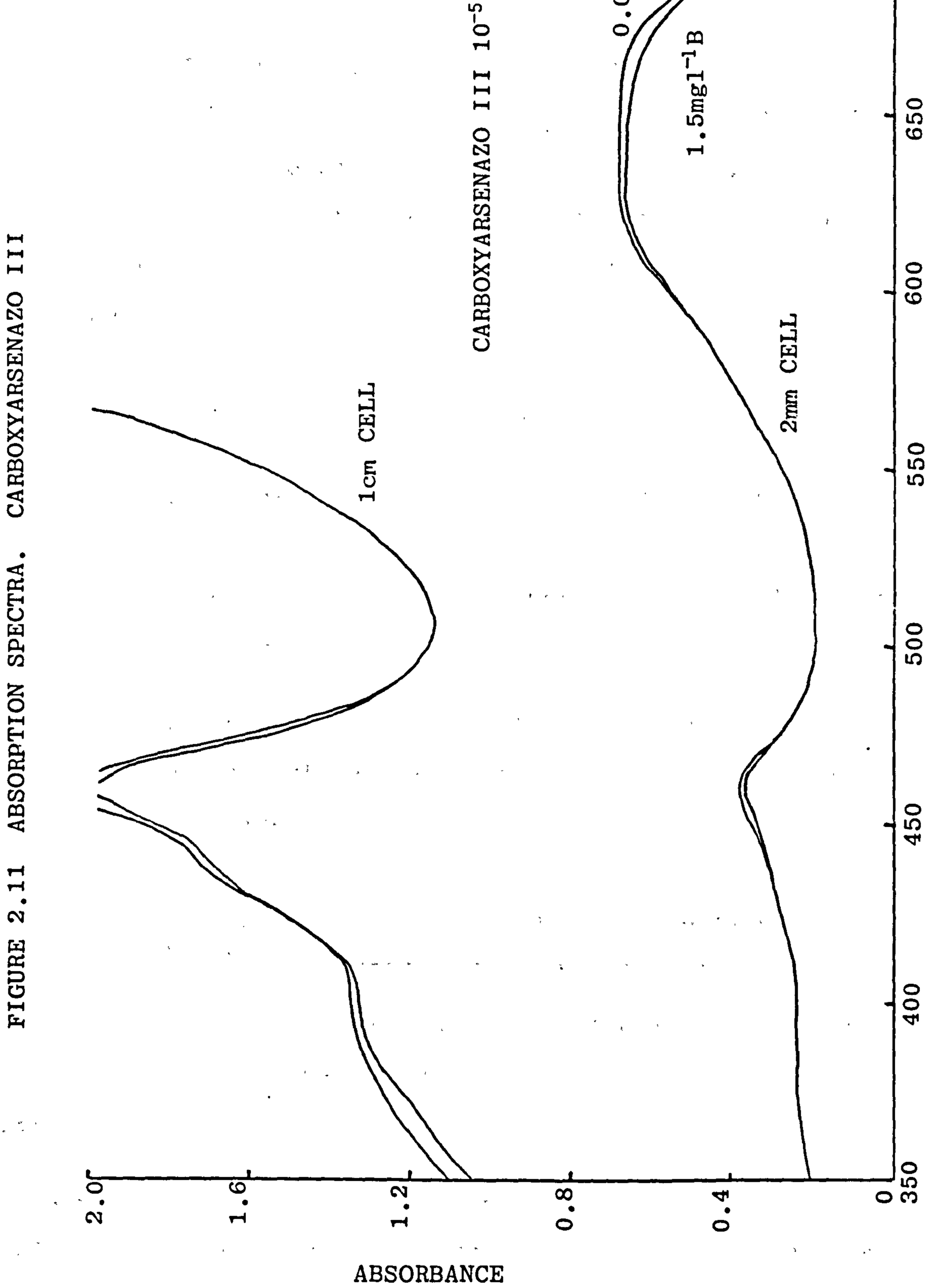


FIGURE 2.10 ABSORPTION SPECTRA. ARSENAZO III FLUORESCENCE SOLUTIONS

FIGURE 2.11 ABSORPTION SPECTRA. CARBOXYARSENAZO III



as the smaller Stokes' shift would require the use of efficient interference filters to approach the discrimination obtained with the dual monochromator instrument used in this work.

Arsenazo III and carboxyarsenazo III may prove suitable for the fluorescence determination of boron at the 10^{-6} - 10^{-7}M level when it would be possible to use more dilute, and less absorbing, solutions of the reagents, but they possess no advantage over thoron which should be usable at these levels if desired.

2.2.4 Purity of arsenophenylazonaphthalene reagents

The paper chromatographic method of Kamata et al.(54) was used to test the purity of these reagents. The developing solvent was composed of a pyridine-ammonia (28% w/w) -1 pentanol mixture in the ratio 10 : 10 : 2.

No impurities were apparent with samples of thoron and arsenazos I and III but several components were present in the sample of carboxyarsenazo III used.

2.2.5 Suitability of reagents examined for determination of boron in steel

The high blank fluorescence associated with resacetophenone limits its usefulness as an analytical reagent for the determination of boron.

Arsenazo I and arsenazo III were found to form fluorescent complexes with boric acid in strong sulphuric acid. This had

not previously been reported, but the small Stokes' shift of the former system and the intense colour of the latter reagent give rise to practical difficulties which are not found when using thoron. This reagent was found to give well separated excitation and emission spectra and to have a linear fluorescent intensity range in excess of the requirements for the determination of boron in steel. Thoron was accordingly chosen as a reagent which merited further investigation.

2.3 Thoron - Establishment of optimum experimental parameters

Initially fluorescence solutions were prepared as in section 2.2.2 when investigating calibration linearity.

(a) Time for development of maximum fluorescence.

Solutions prepared at room temperature reached constant fluorescence after 90 minutes (Figure 2.12).
If the fluorescent solution is not cooled as the aqueous boric acid is 'diluted' with sulphuric acid the heat evolved results in maximum fluorescence being obtained after 60 minutes. Figure 2.13 shows the temperature changes observed during such procedures.

(b) Variation of fluorescence with acid concentration.

Maximum fluorescence was observed when boric acid was dissolved directly in concentrated sulphuric acid. There was little variation in the intensities of fluorescence obtained with acid concentrations between

FIGURE 2.12 DEVELOPMENT OF FLUORESCENCE WITH TIME

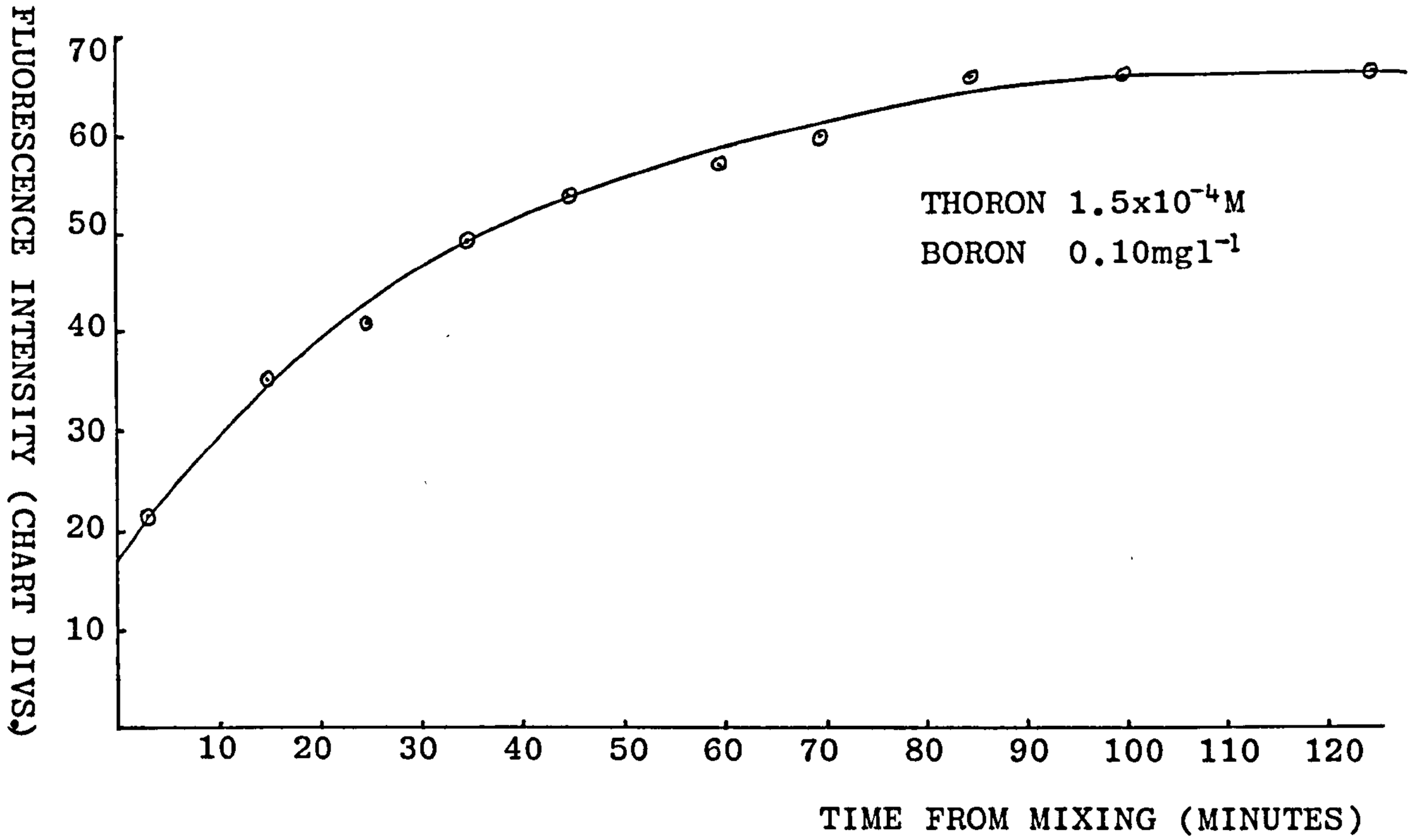
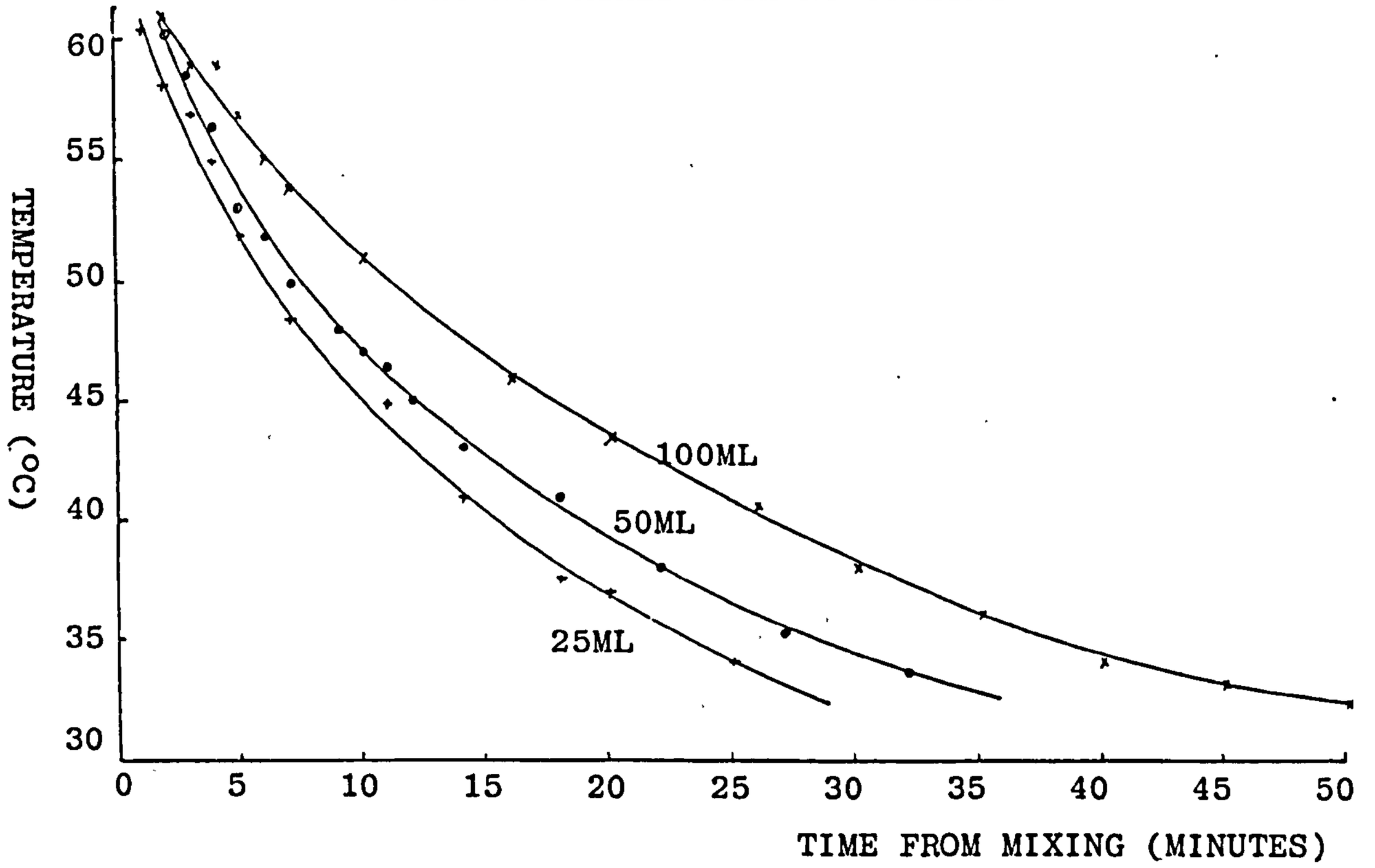


FIGURE 2.13 SOLUTION TEMPERATURES
REAGENTS MIXED WITH NO COOLING



90 and 70% v/v sulphuric acid (Figure 2.14). The heat evolved when preparing 70 and 80% acid concentrations caused practical problems; the solutions required adequate cooling to prevent damage to the container.

(c) Thoron concentration.

Doubling the thoron concentration to 3×10^{-4}M reduced the fluorescence intensity at both excitation peaks. Reducing the concentration by a similar amount to 7.5×10^{-5}M had little effect when fluorescence was excited at 420 nm but gave increased fluorescence with excitation at 476 nm (Figures 2.15, 2.16). These variations arise from the difference in absorption of the fluorescent solution at the two excitation wavelengths as the thoron was present in large excess (0.015mgl^{-1} boron = 1.4×10^{-6}M ; 0.0086% thoron $\simeq$ 1.5×10^{-4}M).

The excitation wavelength of 420 nm is best suited for analytical work as the emitted fluorescence is less affected by changes in the absorption of the measured solution.

(d) Effect of variation of slit widths.

Variation of slit widths had little effect on the relative fluorescence intensities of boron-containing and boron-free solutions (Figure 2.17). Noise levels were reduced as slit widths were increased since more fluorescent radiation was detected and lower amplifier gain (sensitivity) was required. The values chosen - excitation 18 nm, emission 12 nm were the narrowest which gave noise free recorder traces

FIGURE 2.14 THORON - VARIATION OF FLUORESCENCE WITH ACID CONCENTRATION

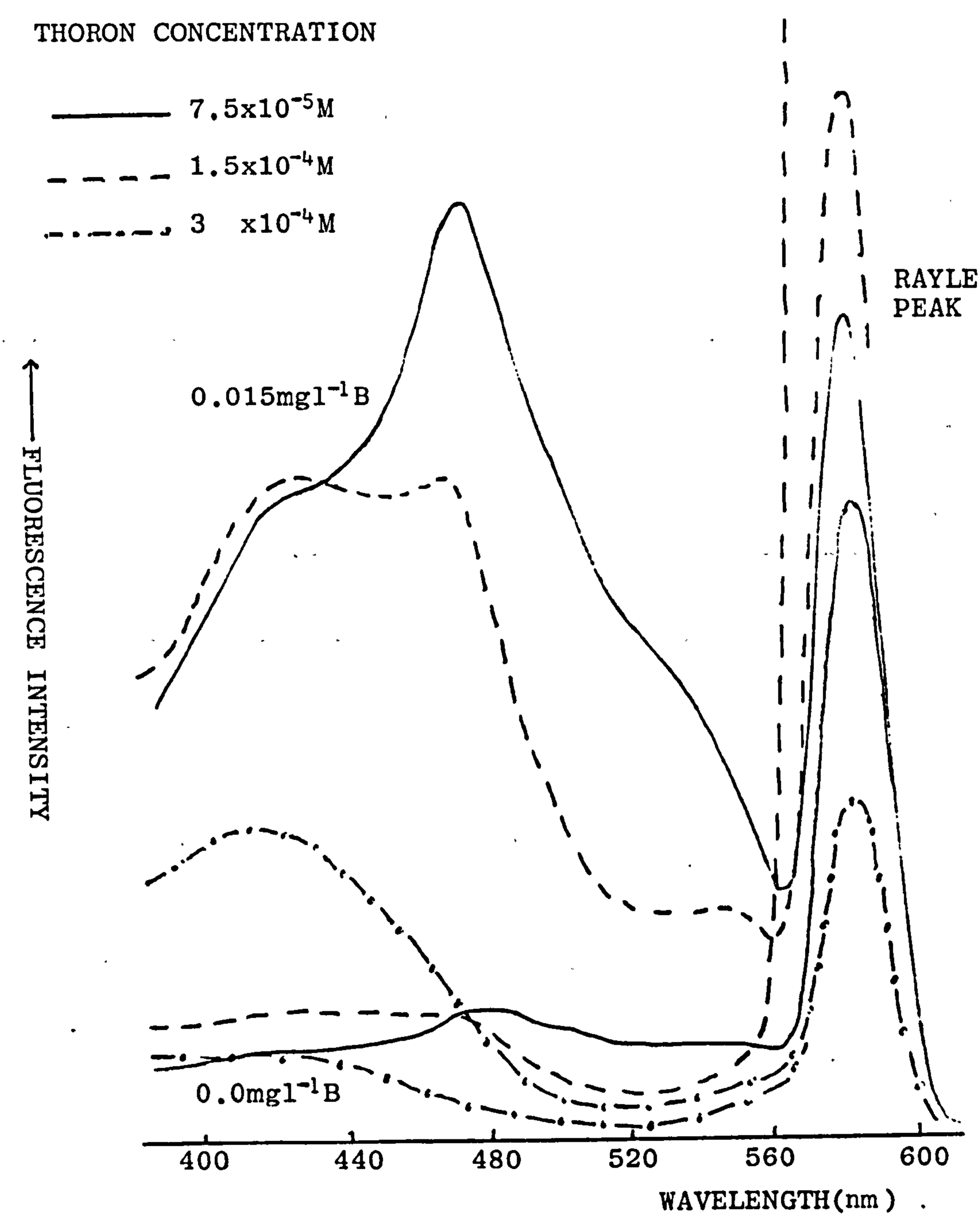
SULPHURIC ACID CONC.(% v/v)	FLUORESCENCE INTENSITY (CHART DIVISIONS)			TRANSMISSION (%)	
	0.01mgl^{-1}B	0.0mgl^{-1}B	DIFF.	420 nm	580 nm
99	54	6	48	17	20
90	34	16	18	8	8
80	27.5	14.5	13	8	4
70	24	10	14	15	10
60	5.5	5	0.5	17	20
50	47	47	0	50	90

FIGURE 2.15 THORON - VARIATION OF FLUORESCENCE WITH THORON CONCENTRATION

λex (nm)	THORON CONC. (10^{-4}M)	FLUORESCENCE INTENSITY (CHART DIVISIONS)			TRANSMISSION (%)	
		0.015mgl^{-1}B	0.0mgl^{-1}B	DIFF.	λex	580 nm
420	0.75	41	6	35	40	55
	1.5	42	8	34	18	30
	3.0	26	5.5	14.5	4	8
476	0.75	58	8	50	12	
	1.5	42	8	34	2	
	3.0	7	2	5	<1	

SENSITIVITY 3 SLITS EX. 18 nm EM. 12 nm

FIGURE 2.16 FLUORESCENCE EXCITATION SPECTRA
VARIATION OF FLUORESCENCE WITH THORON CONCENTRATION



SENSITIVITY 3 SLITS 19 nm EX.
12 nm EM.

FIGURE 2.17 THORON - EFFECT OF VARIATION OF SLIT WIDTH

SLIT WIDTH (nm)		SENSITIVITY	FLUORESCENCE INTENSITY (CHART DIVISIONS)		
EMISSION	EXCITATION				
			0.015mgl^{-1}B	0.0mgl^{-1}B	NOISE
12	30	1	80	13.5	-
	20	2		13.5	-
	16	2		13.7	.1
	12	3		13	.1
	10	3		14	.1
	8	4		14	.1
	4	5		15	.3
30	12	1	80	14	-
20		2		14	-
10		3		14	.2
6		4		14	.4
6	6	6	80	20	.8
26	26	1	80	14	-

λEX. 420 nm λEM. 580 nm

SENSITIVITY - COARSE CONTROL 1 to 6 IN STEPS (SEE APPENDIX 4)
FINE CONTROL 0 to 100 ON CHART RECORDER

SAMPLE FLUORESCENCE SET TO 80 ON CHART IN EACH CASE

The results obtained using thoron are in general agreement with the previous work of Marcantonatos et al, although two peaks were observed in the excitation spectrum and the λ max. values are slightly at variance. The sensitivity is sufficient for the determination of boron in steel. Fluorescence from boron free solutions was low compared to the test solutions and the wavelength difference between the emission band and the excitation wavelength is 160 nm, factors which indicate the possibility of using a simple filter fluorimeter for the determination.

2.4 Development of method for determination of boron in steel

In this section the effect of iron and other elements present in steel on the fluorescence of the thoron - boric acid complex is investigated.

2.4.1 Effect of iron

Solutions containing iron (II) prepared by dissolving high purity iron in sulphuric acid, in addition to boric acid and thoron, showed enhanced fluorescence (Figure 2.18).

The excitation spectrum of the solution containing 1,500mgl^{-1} Fe^{2+} (equivalent to an initial 1% steel solution) was similar to that obtained previously with a decreased concentration of thoron (Figure 2.16 Thoron conc. 7.5×10^{-5}M). The absorption spectrum showed a corresponding decrease in thoron absorption of iron containing solutions (Figure 2.19).

FIGURE 2.18 THORON - VARIATION OF FLUORESCENCE WITH IRON CONCENTRATION

Fe^{2+} CONC (mgl^{-1})	BORON CONC (mgl^{-1})	FLUORESCENCE INTENSITY (CHART DIVISIONS) λEX = 420 nm
1,500	0.15	90
375		86
150		81
0		76.5
1,500	0.075	46
375		45
250		41
0		37.5
1,500	0.0	2
375		1.5
150		1
0		0

λEX (nm)	Fe^{2+} CONC. (mgl^{-1})	FLUORESCENCE INTENSITY (CHART DIVISIONS)			TRANSMISSION (%)	
		0.015mgl^{-1}B	0.0mgl^{-1}B	DIFF	λEX	580 nm
420	4000	73	15	58	50	65
	3000	71	10.5	61.5	48	63
	1500	65	9	56	40	50
476	4000	98.5	15	83.5	22	
	3000	98	13	85	18	
	1500	82	11	71	8	

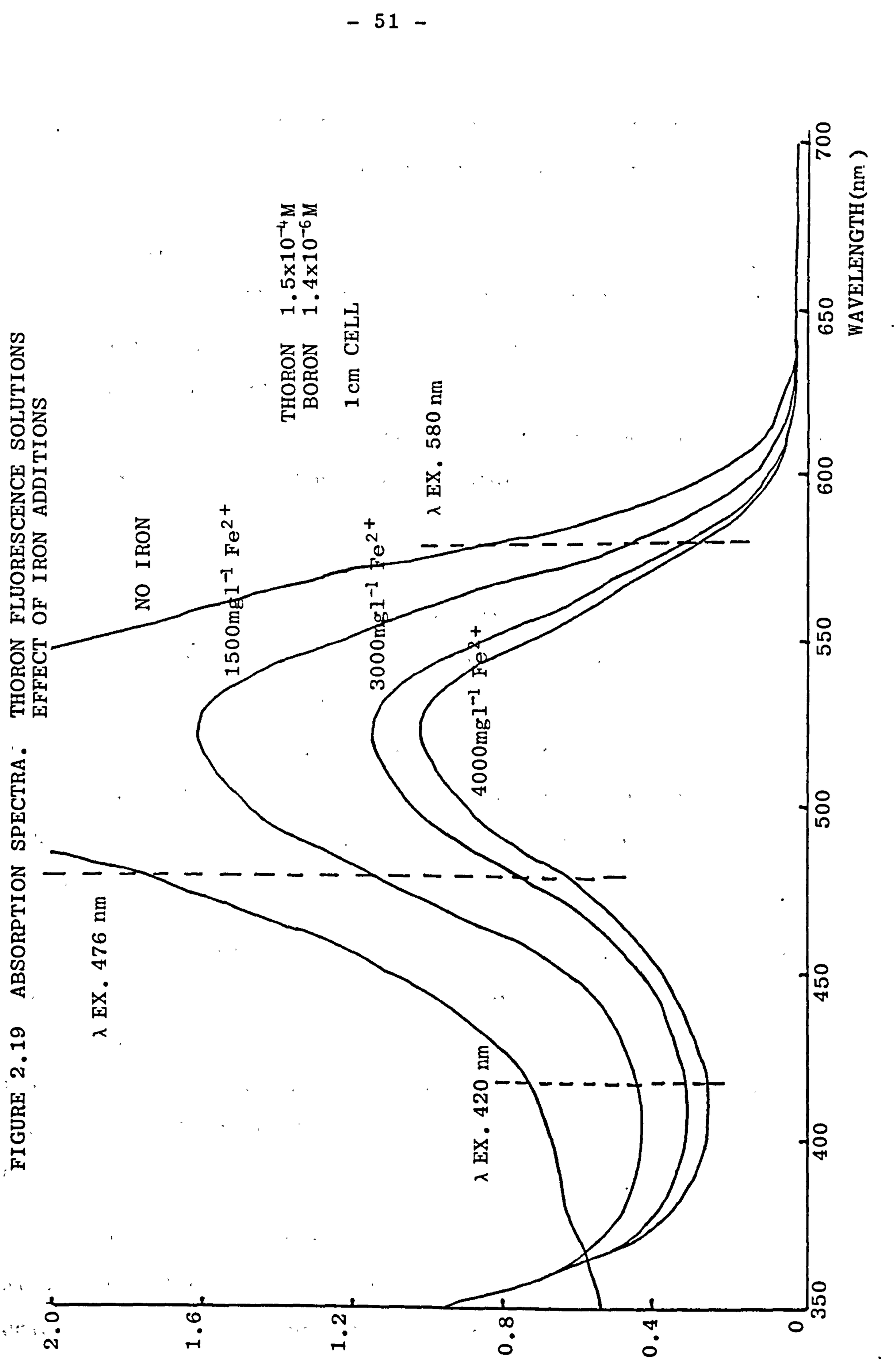


FIGURE 2.19 ABSORPTION SPECTRA.

The emission spectrum was unchanged and the blank fluorescence was unaffected by the addition of iron.

2.4.2 Variation of thoron concentration - solutions containing iron(II)

To assess the necessity of using the thoron reagent in large excess over the boron content, an investigation was made into the effect on fluorescence intensity of varying the amount of thoron present in fluorescent solutions containing iron(II). A range of thoron concentrations from 10^{-5} to 2×10^{-4}M was used while the boric acid concentration was kept constant at either zero or 1.4×10^{-5}M (equivalent to .01% boron in 1% w/v initial steel solution) and the iron concentration was kept at 2.7×10^{-2}M Fe^{2+} (equivalent to 1,500mgl^{-1} in the measured solution or a 1% w/v steel solution). The spectra obtained are shown in Figure 2.20 and the intensities are plotted against thoron concentration in Figure 2.21. Results for iron free solutions are also shown in this figure.

Maximum fluorescence was obtained with a thoron concentration of 10^{-4}M at the excitation wavelength of 420 nm although any fixed concentration between 0.5 and 1.5×10^{-4}M could be used with little decrease in the resultant intensity of fluorescence. Similar results were obtained both with and without the presence of iron.

Greater variation fluorescence was observed with excitation at 476 nm. The fluorescence decreased above 5×10^{-5}M thoron coinciding with the decrease in transmission of the fluorescent

FIGURE 2.20 VARIATION OF FLUORESCENCE WITH THORON CONCENTRATION

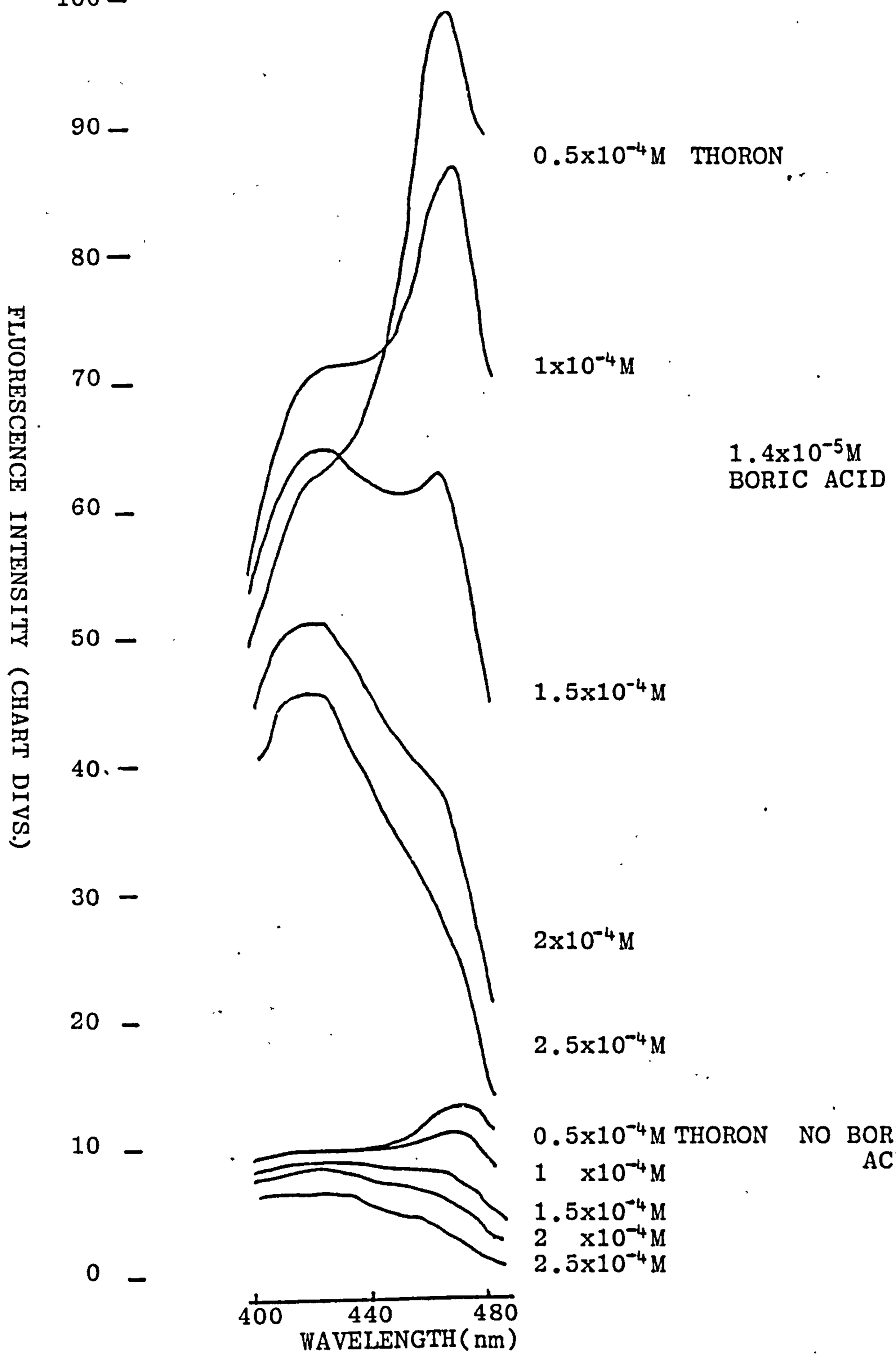


FIGURE 2.21 VARIATION OF FLUORESCENCE WITH THORON CONCENTRATION

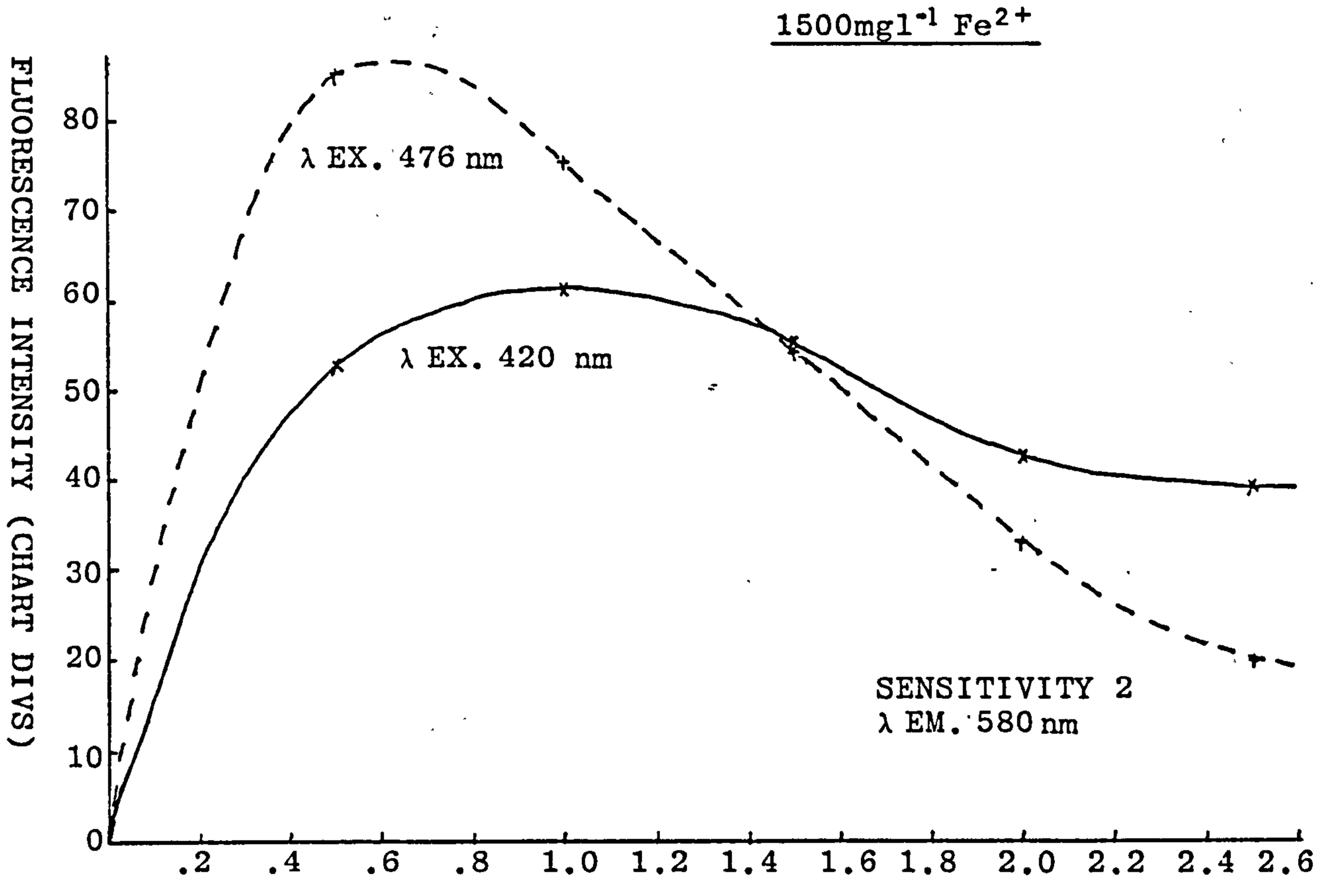
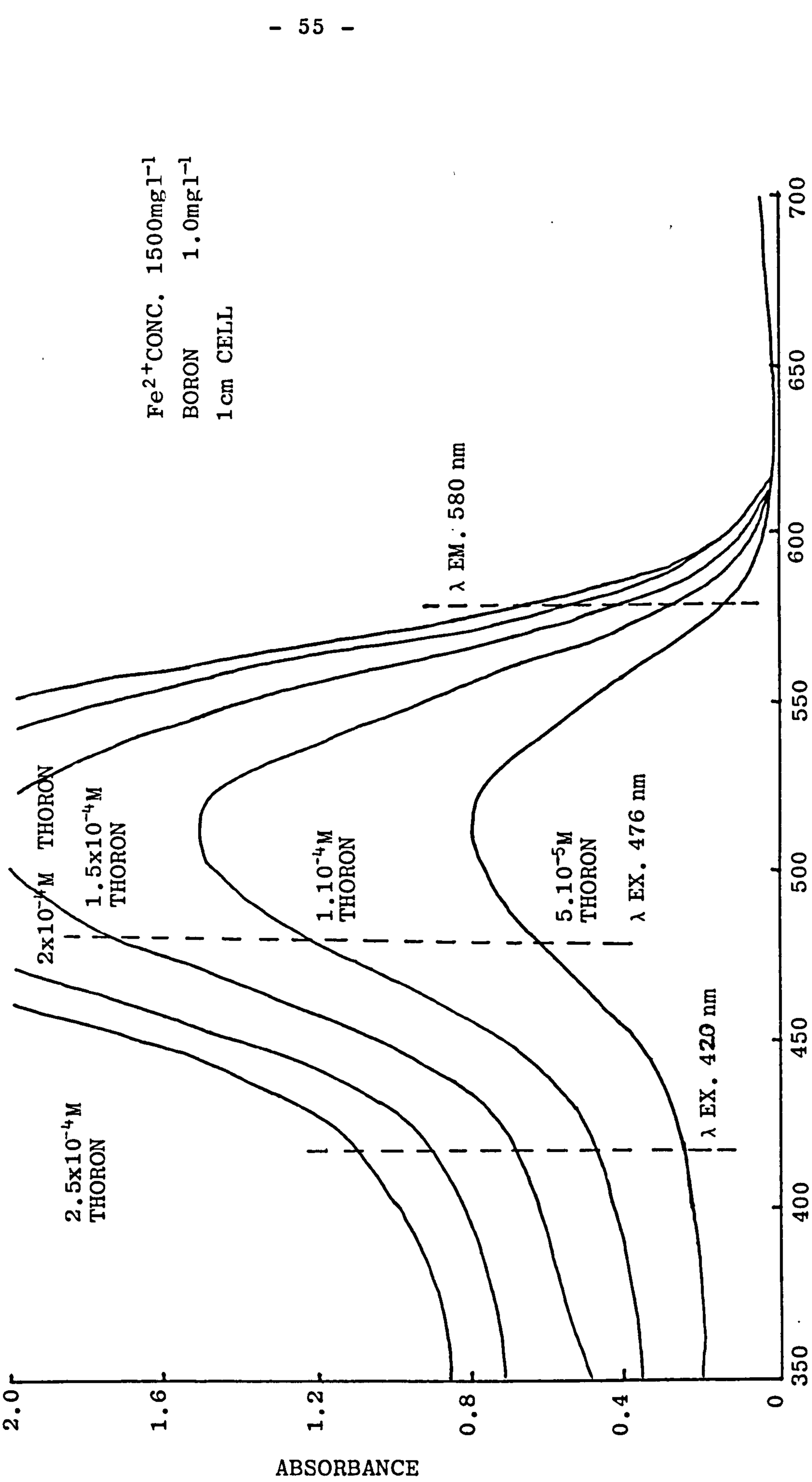


FIGURE 2.22 VARIATION OF ABSORBANCE WITH THORON CONCENTRATION



solution. At 2×10^{-4}M thoron concentration the transmission at 476 nm was significantly less than 1% and no fluorescence peak was observed at this wavelength (Figure 2.22). It was also noted that the thoron solutions used in this investigation were more deeply coloured than solutions of similar concentrations used in the previous section. This is apparent from comparing Figures 2.22 and 2.19. This may be attributed to the thoron stock solution darkening on standing. The effect on fluorescence intensity, though small, is more pronounced when the excitation wavelength was 476 nm than when 420 nm was used.

2.4.3 Time for formation of complex - solutions containing iron

Boron solutions containing iron(II) were found to reach maximum fluorescence in similar times to iron free solutions (Figure 2.23) but solutions containing iron(III) reached a maximum in about a third of the time. The intensity was however much reduced although the transmission of solutions with iron(II) and iron(III) added was similar at the excitation wavelength (420 nm).

2.4.4 Effect of constituents of steel solution - other than iron

High purity chromium, nickel, molybdenum and titanium metals were dissolved in 30% v/v sulphuric acid and used to prepare boron-containing and boron-free solutions for fluorescence measurement as previously described.

Chromium, nickel and molybdenum additions had little effect

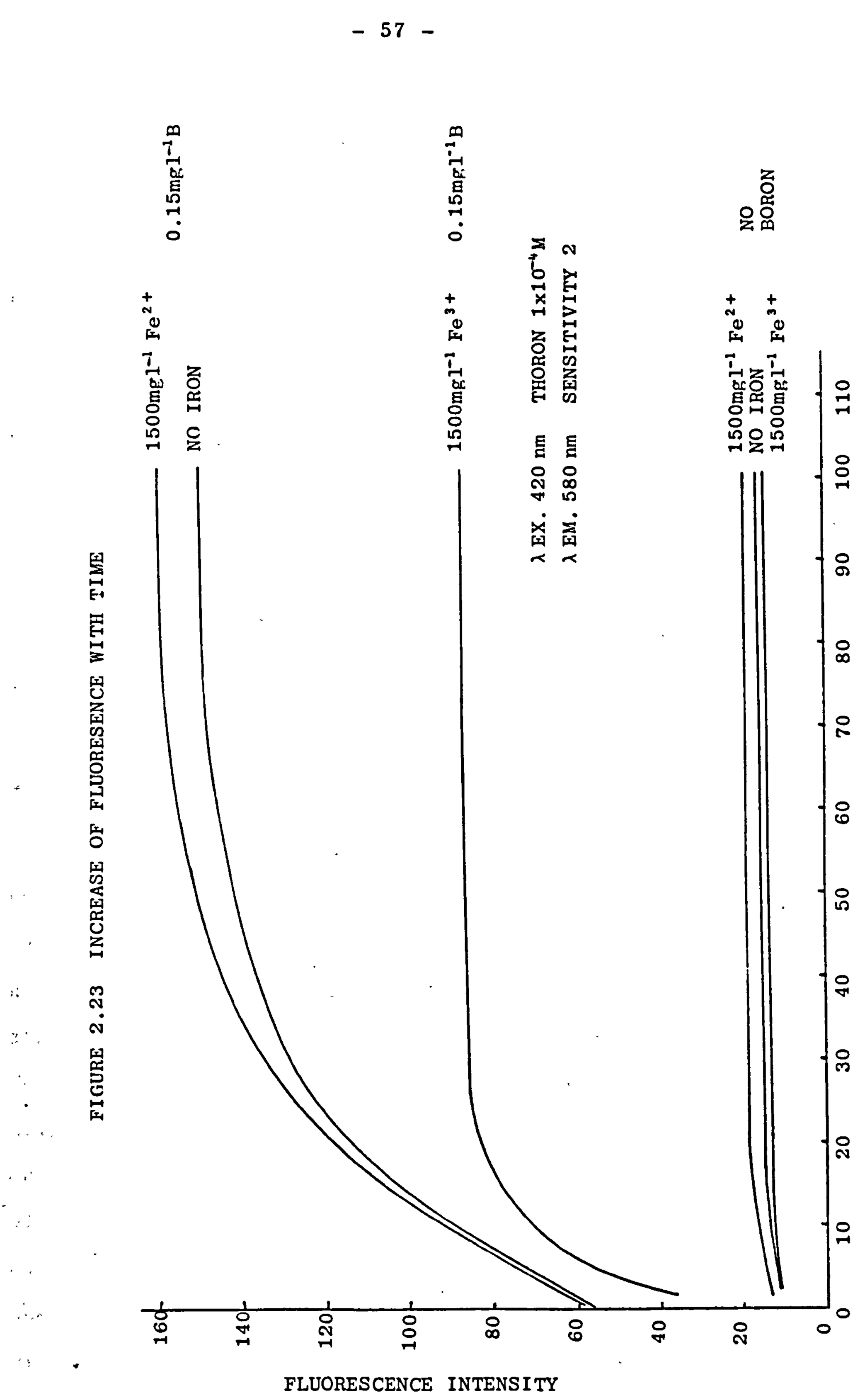


FIGURE 2.23 INCREASE OF FLUORESCENCE WITH TIME

on fluorescence intensity even when present in amounts well in excess of those found in mild and low alloy steels (Figure 2.24).

Titanium at 25mgl^{-1} caused little interference. This is an amount equivalent to 1.6% in an initial 1% steel solution and is above the level found in all but specialized high alloy steels. Above this level the thoron reagent was progressively decolourized giving initially an increase in fluorescence intensity from the boron complex (similar to the effect observed with iron(II)) and then to a diminution as the reagent was destroyed. This effect was less apparent in the presence of iron (Figure 2.25).

Sodium carbonate additions in amounts required for fusion of insoluble compounds gave no change in fluorescence.

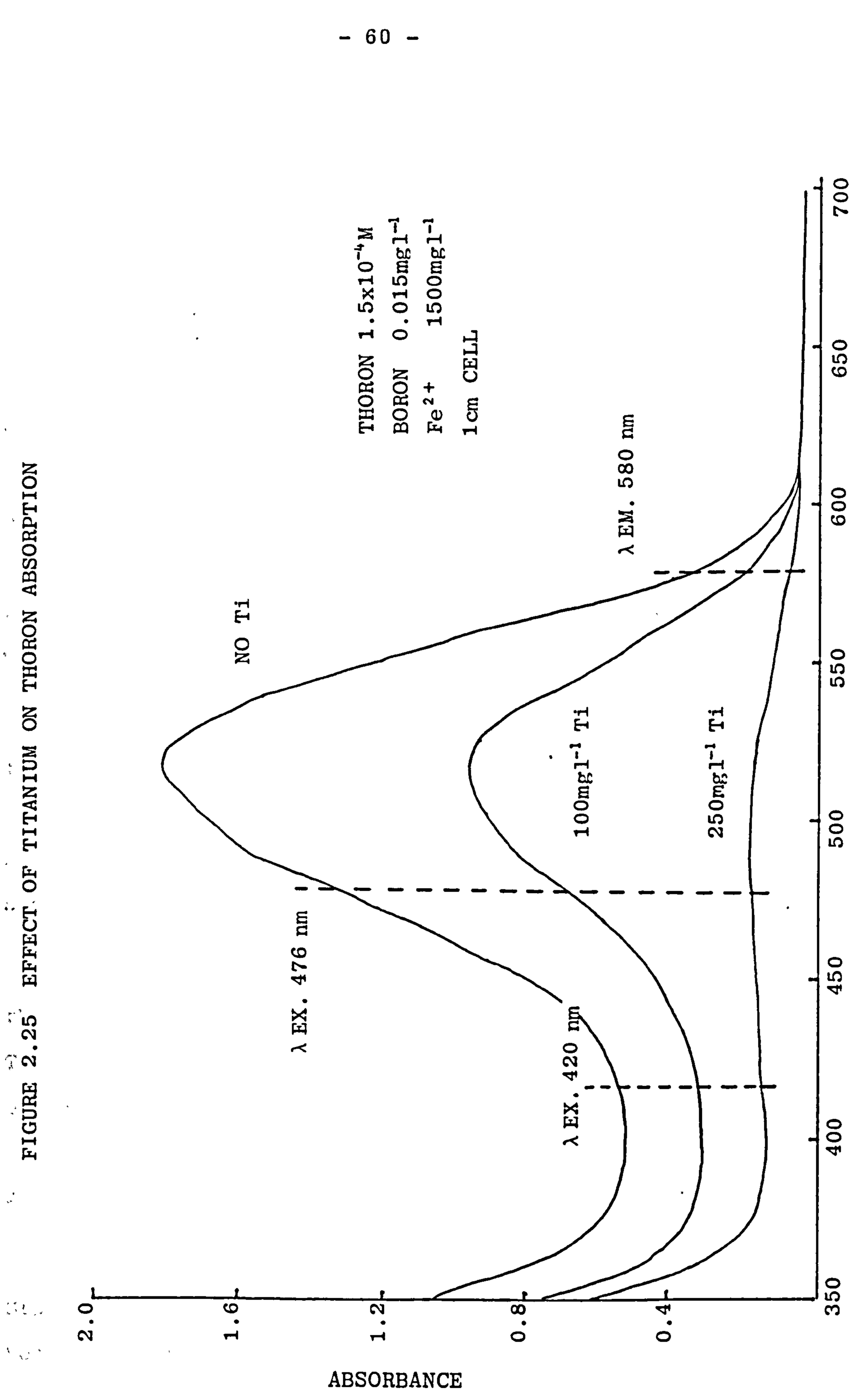
2.4.5 Summary

An excess of thoron is required for maximum fluorescence but the presence of iron(II) has no significant effect on the size of the excess required. Excitation at 420 nm is less affected by changes in thoron concentration and solution absorption than with excitation at 476 nm and is preferred for analytical work. Although the resulting fluorescence is slightly lower, this is not a problem at the levels of boron encountered in steels. Similarly the optimum concentration of thoron was found to be 10^{-4}M but there is little loss of sensitivity using concentrations from 0.5 to 1.5×10^{-4}M. At the latter concentration excitation bands at 420 and 476 nm are of similar intensity and this concentration was chosen for subsequent work.

FIGURE 2.24 THORON - VARIATIONS OF FLUORESCENCE WITH VARIOUS CATIONS

CATION	ADDITION		FLUORESCENCE INTENSITY ($0.01 mg l^{-1}$) (CHART DIVISIONS)	TRANSMISSION (%)	
	$mg l^{-1}$ MEASURED SOLUTION	EQUIVALENT % IN SOLID STEEL SPL.		420 nm	580 nm
-	-	-	13.5	20	20
Cr^{III}	100	6.7	13	20	20
	500	33	18.5	20	20
Ni^{II}	500	33	13	20	20
Mo^{IV}	250	17	17	20	20
Ti^{III}	25	1.6	13.5	20	20
	100	6.7	25	50	50
	250	17	2.5	80	80
Fe^{II}	1500	100	56	40	50
Fe^{II} + Ti^{III}	1500	100	55	45	63
	100	6.7			
Fe^{II} + Ti^{III}	1500	100	45	70	85
	250	17			
Fe^{II} + (Na_2CO_3)	1500	100	55	30	45
	1500	(10gpl)			

FIGURE 2.25 EFFECT OF TITANIUM ON THORON ABSORPTION



Iron(II) was found to cause enhanced fluorescence from the boric acid - thoron complex which was related to the decreased absorption of the solutions.Iron(III) additions produced a decrease in fluorescence which could not be related to the absorption of the sample solution.

In the determination of boron in steel calibration and sample solutions would need to be matched for iron content and its oxidation state. The method used for preparation of solutions ensures that iron is present as iron(II) and the change in fluorescence caused by iron(II) at the levels found in steels is small enough that variation in iron contents of various steels would be insignificant.

The initial investigations did not show any serious interference from alloying elements commonly found in steels. Titanium reacted with thoron destroying the reagent but caused no interference when present at levels encountered low alloy steels.

There appears to be no constraint to the application of the method to the direct determination of boron in steel samples. The proposed fluorimetric procedure for the determination of boron in steel is given in appendix 1.

2.5 Fluorimetric determination of boron in steel using thoron

Two series of solutions were prepared from British Chemical Standard steels dissolved in sulphuric acid (30% v/v) by gentle heating and using a modification of the procedure of Harrison

and Cobb (55) in which the acid insoluble boron was fused with sodium carbonate, dissolved in sulphuric acid (30% v/v) and added to the soluble portion. The dissolution procedure is detailed in appendix 1.

The fluorescence measurements for each solution were plotted against the certificated boron contents. The line of best fit through these points gave deviations from these values which were in no case larger than the spread of the individual results quoted on the certificate for each standard, shown on the graph as a horizontal line (Figures 2.26, 2.27).

A more rigorous test of the procedure was carried out using synthetic standards prepared from pure boron free iron samples (<.0001%B) to which known amounts of boric acid in sulphuric acid (30% v/v) were added during the dissolution stage. The calibration graph prepared from these standards was used to obtain boron contents of five separate samples of each of two BCS steels which had been taken through the complete dissolution, fusion and fluorimetric procedures (Figure 2.28). The calibration obtained was linear and the mean result of both BCS steels agreed well with the certified values (which were only quoted to the nearest .001% boron). The spread of results was ±.0003% at 0.007% boron and ±.0001% at 0.003% boron.

It is more convenient to construct the calibration graph from synthetic boric acid - iron solutions as the fusion procedure which involves the use of platinum ware is not required and the time to complete a determination is thus decreased.

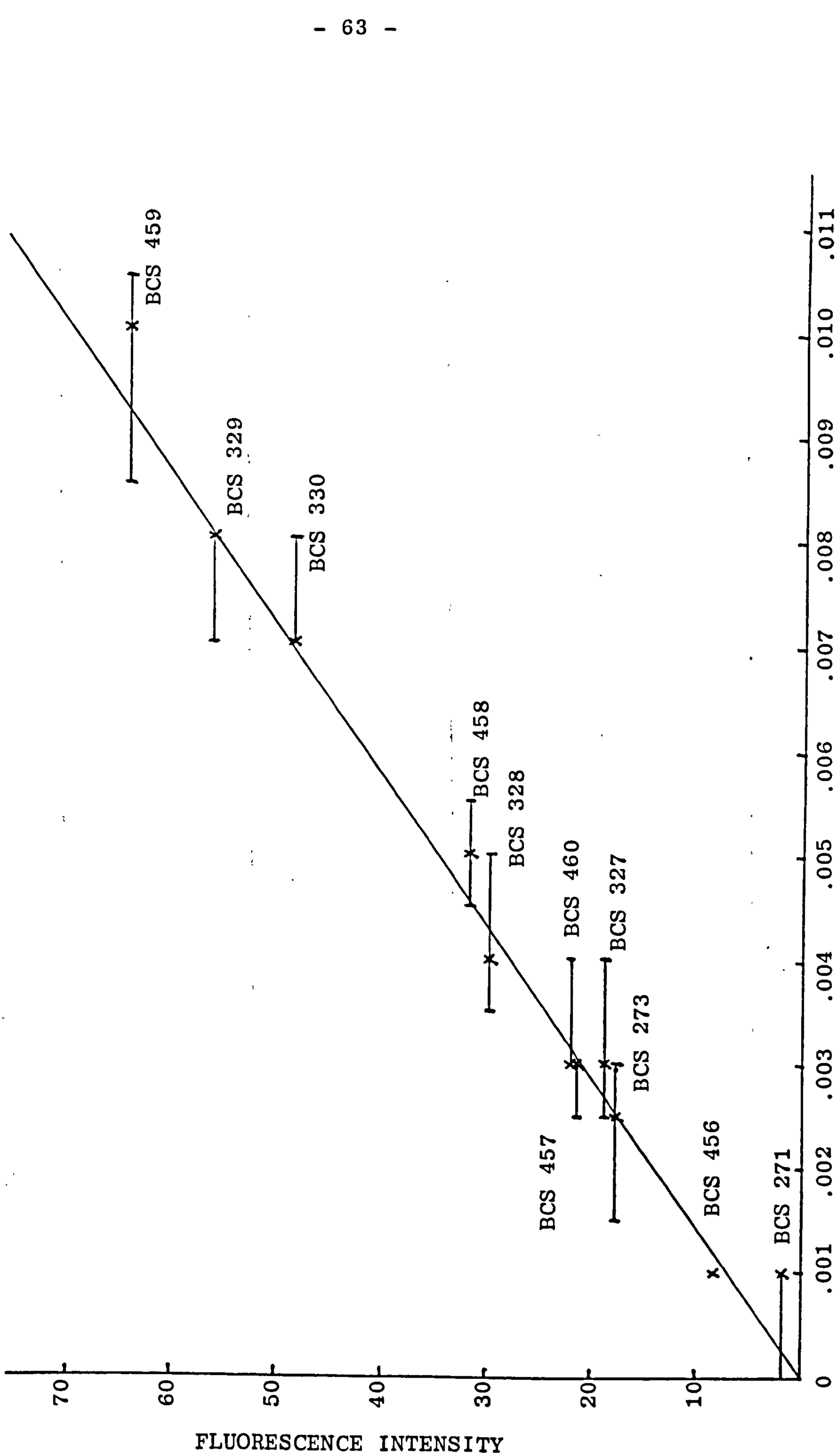


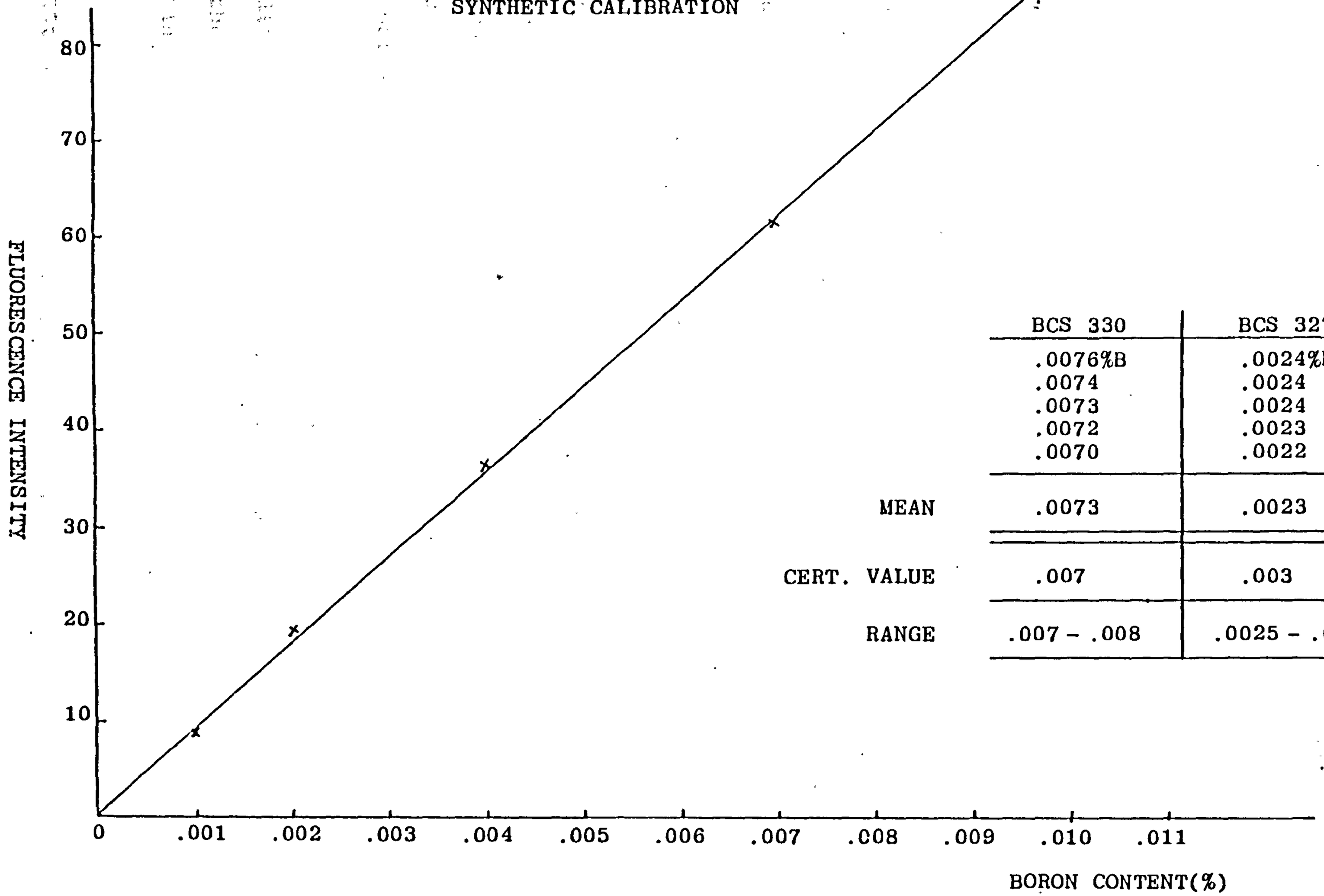
FIGURE 2.26 CALIBRATION GRAPH PREPARED USING BCS STEELS

FIGURE 2.27 RESULTS OF CALIBRATION USING BCS STEELS

BCS No	CERTIFICATE VALVE(%B)	CERTIFICATE RANGE(%B)	EXPERIMENTAL RESULT		DIFFERENCE FROM CERT.
			SERIES 1	SERIES 2	
277	<.001	<.001	.0003	.0002	-
273	.002	.0015-.003	.0025	.0026	+.0005
271	.013	.010 -.016	.0135	.0139	+.0007
326	.001	.001	.0013	.0012	+.0002
327	.003	.0025-.004	.0026	.0023	-.0006
328	.004	.0035-.005	.0043	.0043	+.0003
330	.007	.007 -.008	.0069	.0068	-.0002
329	.008	.007 -.008	.0080	.0084	+.0002
456	.001	.0010	.0012	.0010	+.0001
457	.003	.0025-.0030	.0030	.0030	-
460	.003	.003 -.004	.0031	.0032	+.0002
458	.005	.0045-.0055	.0046	.0043	-.0006
459	.010	.0085-.0105	.0091	.0091	-.0009

FIGURE 2.26 ILLUSTRATES RESULTS FROM SERIES 1

FIGURE 2.28 FLUORMETRIC DETERMINATION OF BORON IN STEEL
SYNTHETIC CALIBRATION



	BCS 330	BCS 327
	.0076%B	.0024%B
	.0074	.0024
	.0073	.0024
	.0072	.0023
	.0070	.0022
MEAN	.0073	.0023
CERT. VALUE	.007	.003
RANGE	.007 - .008	.0025 - .004

An opportunity arose during this work to apply the proposed method to the standardization of a BCS certified reference material - an austenitic stainless steel. A calibration graph was prepared by making boric acid additions to a stainless steel of low boron content (.0003% boron) - a similar procedure to the synthetic calibration described above but using stainless steel in the place of pure iron. The mean value of four separate determinations was identical to that obtained from a similar number of determinations using the circumin colorimetric procedure (4) and was within 0.001% boron of the final certified value. The issued certificate of analysis is appended (Appendix 2).

The time for sample dissolution and fusion was similar for both fluorimetric and colorimetric procedures but whereas the calibration standards and samples for fluorescence measurement can be prepared in a single batch, only one distillation of methyl borate, required in the colorimetric procedure, can be performed at a time. The time taken for distillation and subsequent evaporation of the distillate for a batch of determinations is thus far greater and the procedure is more labour intensive than that of the fluorescence method where solutions can be prepared and set aside until fluorescence has developed.

Although the fluorimetric procedure required care when handling concentrated sulphuric acid the circumin reagent used in the colorimetric method is dissolved in glacial acetic acid and in practice is just as objectionable in use.

The colorimetric procedure has a lower range limit of 0,0005% boron. The fluorimetric procedure at this level was

using instrumental sensitivity setting 2 (of 6), a further 80 fold increase in sensitivity was available with the MPF2A fluorimeter (see Appendix 4). The lower-limit of detection using the fluorimetric procedure would be governed by contamination from reagents and apparatus rather than the sensitivity of the procedure.

The proposed fluorescence procedure for the determination of boron in steel using thoron has been successfully applied to the analysis of thirteen BCS low allow or mild steels - showing that elements present in minor amounts in steel to not affect the determination.

It has been shown that calibration with solutions prepared from boric acid and iron give results in agreement with certified values for BCS steels and which have comparable reproducibility to those obtained from the much longer British Standard method:-

Fluorescence	at 0.0023%B the range was	±0.0001%B
	at 0.0073%B the range was	±0.0003%B
British Standard	at 0.0025%B 2sw =	±0.0002%B
	at 0.0075%B 2sw =	±0.00036%B

An unknown sample (an unstandardized BCS steel) was analysed and the result obtained (0.0024%B) found to be 0.001% boron from the 'true' (i.e. the final certificated) value.

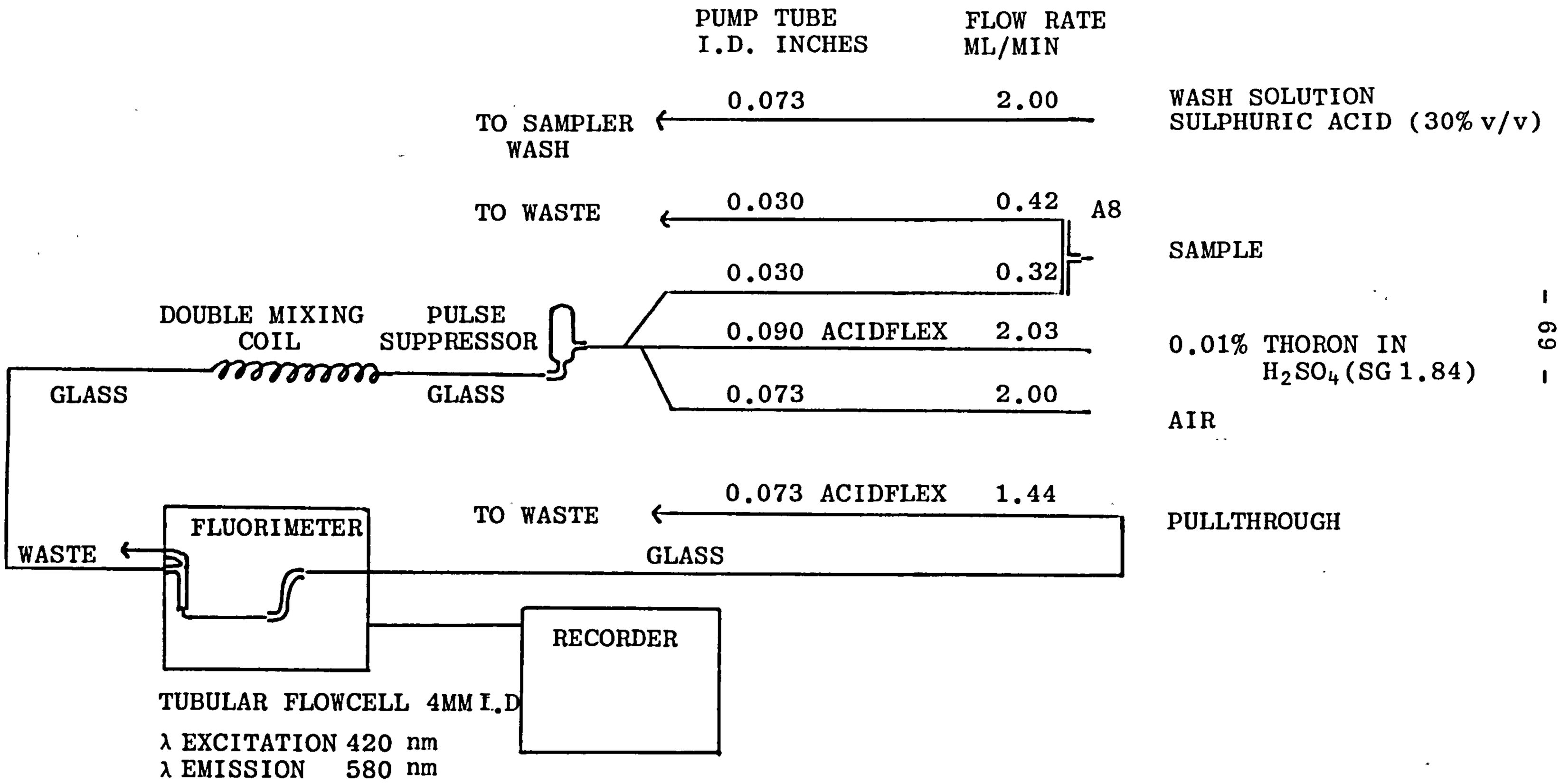
2.6 Automation of thoron fluorimetric procedure

Experience gained using the Technicon Auto Analyzer for colorimetric analysis of steelworks materials suggested that the equipment could be used in conjunction with a fluorimeter for the determination of boron.

Although sample solution preparation would of necessity be manual, the later stages of the analysis could be automated. The 'manifold' (the assembly of tubing, glass coils etc. from peristaltic pump to fluorimeter) which was developed is illustrated schematically in Figure 2.29.

In designing the portion of the manifold where concentrated sulphuric acid (the solvent for thoron) is mixed with an aqueous solution (the sample - 30% v/v sulphuric acid) great care needed to be exercised to ensure that the pumping rate remained regular. If this was not the case each liquid segment could contain a different ratio of acid to water and on de-bubbling these liquid segments stratified layers would be formed in the flowcell resulting in noisy recorder traces. To ensure that this did not occur, the sample stream was split so that no change of flow occurred during sample changes due to entrained air, a pulse suppressor was incorporated into the flow system to produce an even flow as the sample and reagent meet and glass tubing was used in preference to the acid resisting acidflex tubing (a fluorinated rubber) when possible. The tubing lengths were in any case kept as short as possible.

FIGURE 2.29 AUTOANALYSER FLOWSYSTEM FOR BORON IN STEEL



The light source of the Auto Analyzer colorimeter was not intense enough to be used to excite detectable fluorescence, so the automated system was connected to a 1cm square fluorimeter flowcell mounted in the Perkin - Elmer MPF-2A spectrofluorimeter. This was only partially successful because the geometry of the flowcell, while suitable for use with an automated filling and emptying device, was unsatisfactory when used with a continuous flow system. The capacity of the cell was large in relation to the flow rate, the inflowing sample solution did not immediately displace the previous sample or wash and a recirculating flow within the cell led to considerable intermixing of samples. It was therefore impossible to obtain a steady trace when continuously pumping sample solution.

A flowcell was constructed from Pyrex tubing (4mm i.d.). The transmission range of this glass (320 - 1000 nm) was suitable for the excitation and emission wavelengths used in the fluorimeter procedure. The flowcell was mounted vertically as shown in Figure 2.30. This arrangement gave much reduced noise levels and a significant gain in sensitivity compared with the manual procedure, where the static solution is measured in a standard 1cm cell, in spite of the smaller volume of the flowcell. This may be attributed to the cell being placed accurately at the focus of the incident radiation and to decreased absorption losses in the smaller cell. The gain is all the more significant when the time for development of fluorescence is taken into account. The period of residence in the flow system, when one double length mixing coil was used, allows only 8½ minutes for

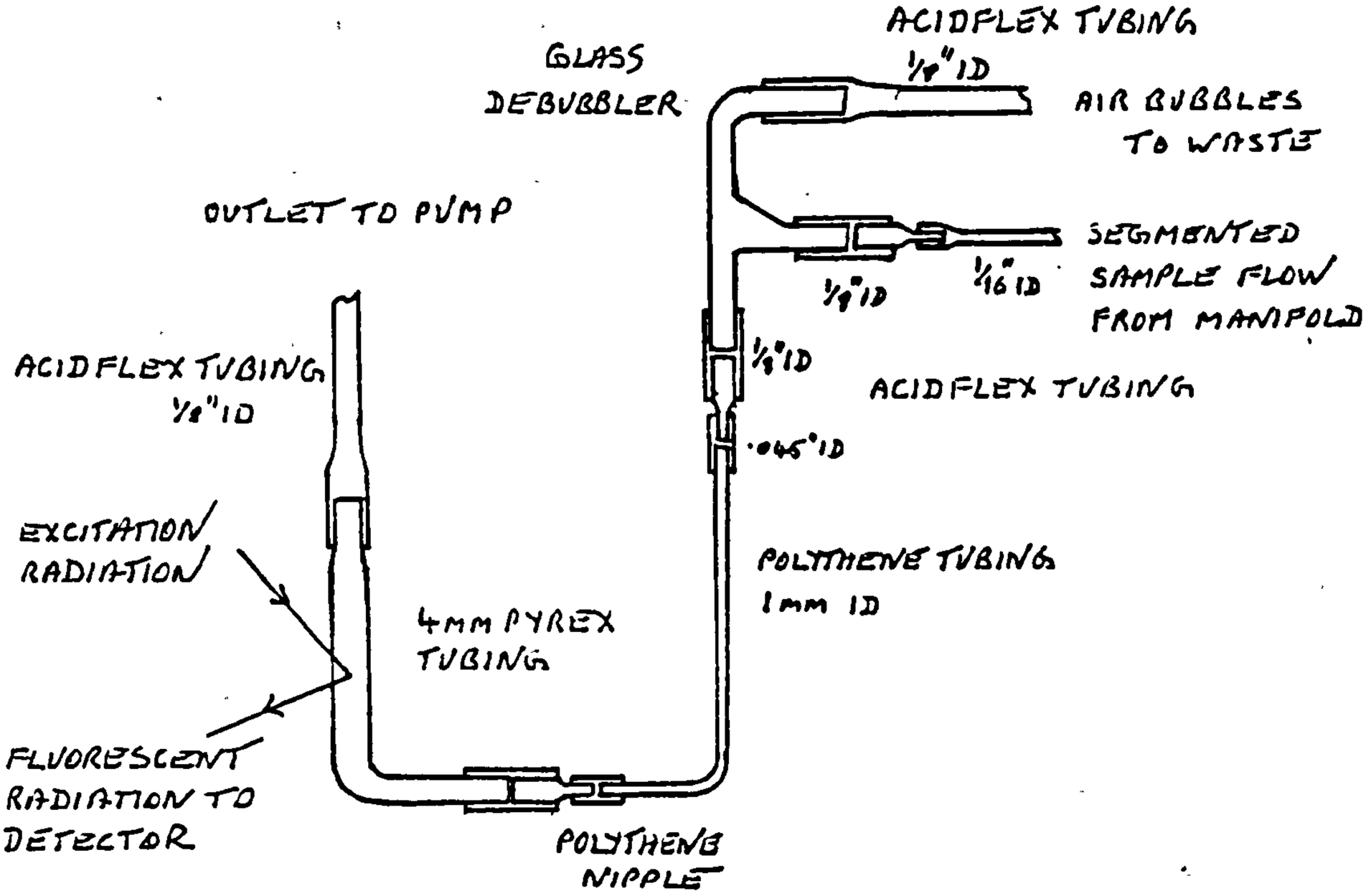


FIGURE 2.30 FLOWCELL AND ASSOCIATED COMPONENTS MOUNTED IN FLUORIMETER CELL COMPARTMENT

the development of the fluorescence compared with the optimum time of 90 minutes used in the manual method.

A synthetic steel solution equivalent to 0.002% boron gave a noise level of ±1.5 scale divisions when the fluorescence signal was set to give a full scale reading. This corresponds to an uncertainty of less than ±0.00005% boron.

The automated procedure gave satisfactory results with a number of BCS steel samples and synthetic steel calibration standards. A typical chart output is shown in figure 2.31 and the calibration graph and results derived from this chart in figure 2.32. The results and their spread are similar to those obtained with the manual method.

2.6.1 Investigation of interferences using the automated procedure

The development of the automated fluorimetric procedure facilitated a more comprehensive investigation of likely interferences. A controlled concentration gradient technique was used for this investigation - concentrated solutions of various high purity metals in sulphuric acid (30% v/v) containing a fixed amount of boron were added at a constant rate to a pure solution of boric acid in sulphuric acid (30% v/v) of the same boron content using the AutoAnalyzer peristaltic pump. The solution to which the metal-containing solution was being added was 'sampled' at the same rate as the addition so that its volume remained constant. (Figure 2.33). A portion of this sample was used for the automated fluorimetric procedure.

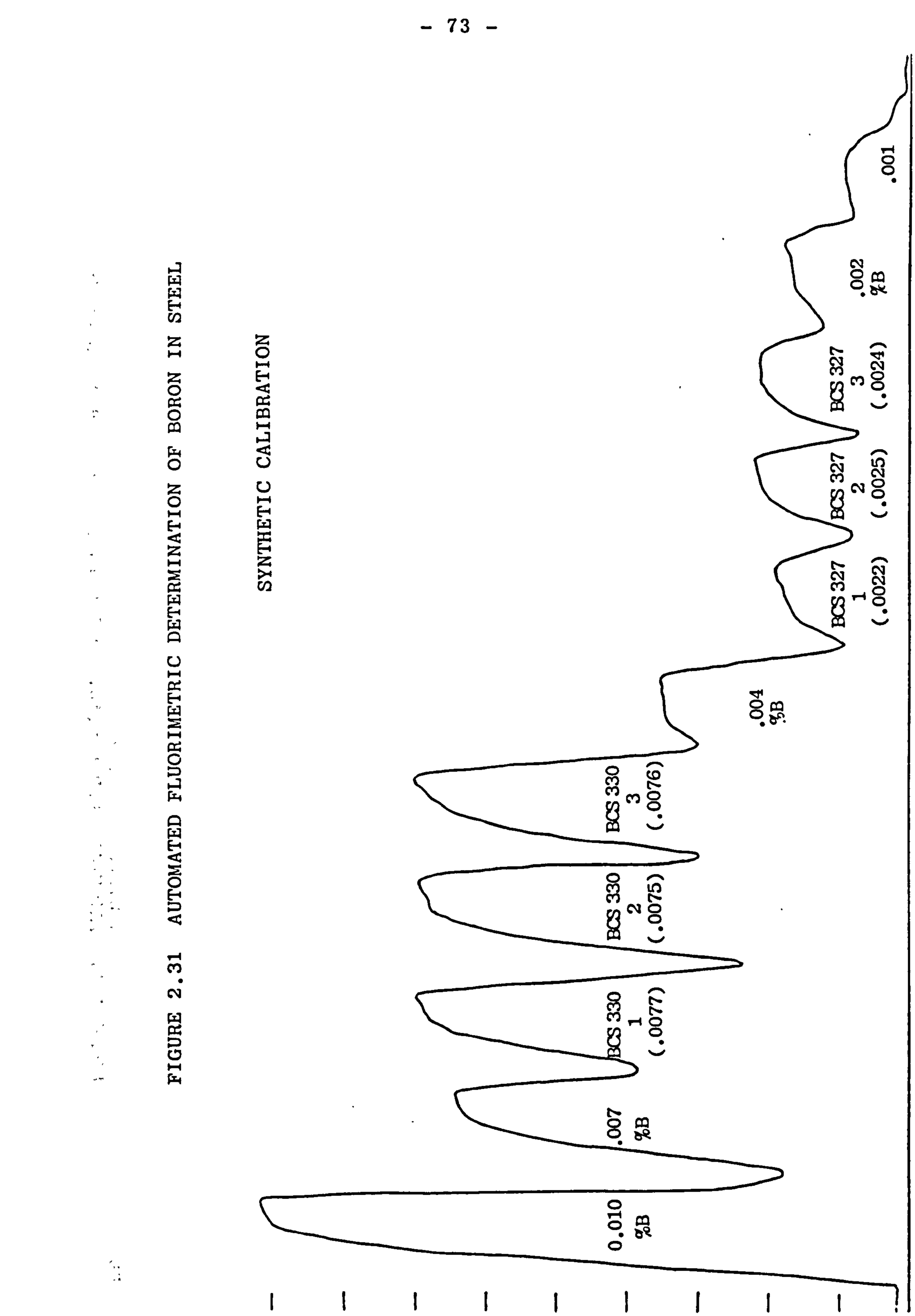


FIGURE 2.31 AUTOMATED FLUORIMETRIC DETERMINATION OF BORON IN STEEL

BCS 327
.0025%B
.0024
.0022
.0024
.003
.0025 - .004

BCS 330
.0077%B
.0076
.0075
.0076
.007
.007 - .008

MEAN

CERT. VALUE

RANGE

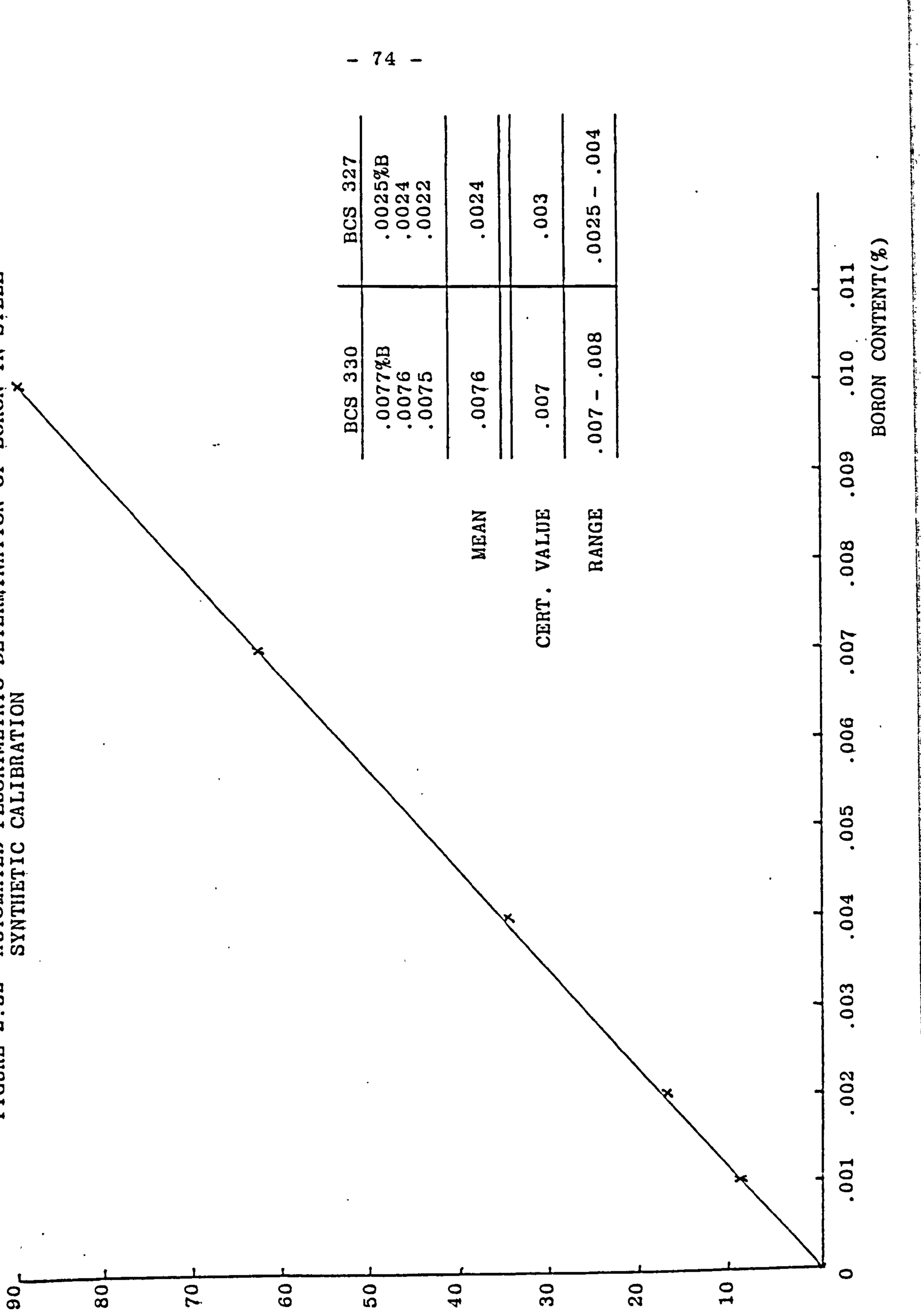


FIGURE 2.32 AUTOMATED FLUORIMETRIC DETERMINATION OF BORON IN STEEL
SYNTHETIC CALIBRATION

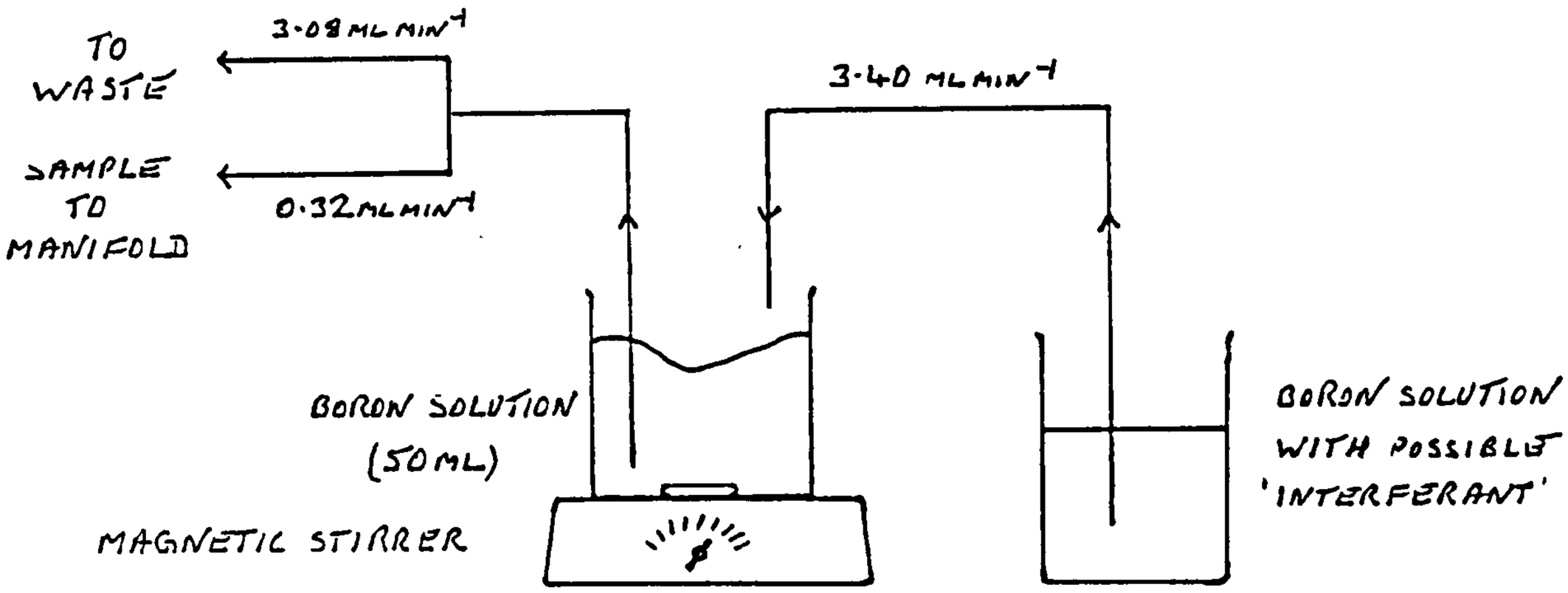


FIGURE 2.33 ASSEMBLY FOR CONTROLLED CONCENTRATION GRADIENT

The concentration of the added metal at a given time, C_t, when the initial concentration in the mixing vessel is zero, is given by the formula

$$C_t = C_L(1 - e^{-Rt/V})$$

where C_L is the concentration of 'interferant' in the added solution;

C_t is the concentration after time t mins in the mixed solution;

R is the flow rate (3.4ml min^{-1})

V is the initial volume (50ml)

$$C_t = C_L(1 - e^{-3.4t/50})$$

and if $C_t = \frac{1}{2}C_L$ at time $t_{\frac{1}{2}}$

$$t_{\frac{1}{2}} = 0.693 \times \frac{50}{3.4}$$

$$= 10.2 \text{ mins.}$$

A 'blank' controlled concentration gradient experiment was performed initially. A solution containing 0.4mgl^{-1} boron (corresponding to 0.004% in a steel sample) was used as both sample and 'interferant' solution. At time $t_{\frac{1}{2}}$, the time for half the sample solution to have been replaced by interferant, the fluorescence level remained unchanged. Changes in fluorescence equivalent to 0.0001% boron should therefore be noticeable.

From the trace of fluorescence intensity versus time values of intensity can be read off at times corresponding to specific concentrations of the added interferant. This is illustrated

for chromium additions in figure 2.34. The results of this work are shown in the table - figure 2.35.

The addition of iron produced less effect on fluorescence in the automated procedure than with the manual method. With the smaller volume of the flowcell there are correspondingly less absorption losses and the emitted fluorescence is less affected by changes in the transmission of the solution.

Chromium at levels encountered in low alloy steels had no significant effect. At the levels found in stainless steels both blank and sample solutions were affected by similar amounts. At still higher levels (above 20% Cr) the nett fluorescence intensity due to boron decreased as the colour of the solution deepened. Titanium also produced negative deviations of blank and sample solutions, at high levels the reagent was progressively decolourized. As with chromium additions, the amounts encountered in low allow steels produced no significant effect.

Additions of 5% v/v phosphoric or perchloric acids to the sample solutions produced no change in blank fluorescence but no fluorescence due to boron was obtained from sample solutions. Hydrochloric and nitric acid additions decolourized the reagent and no fluorescence was observed. It thus appears that sulphuric acid is the only suitable medium for complex formation.

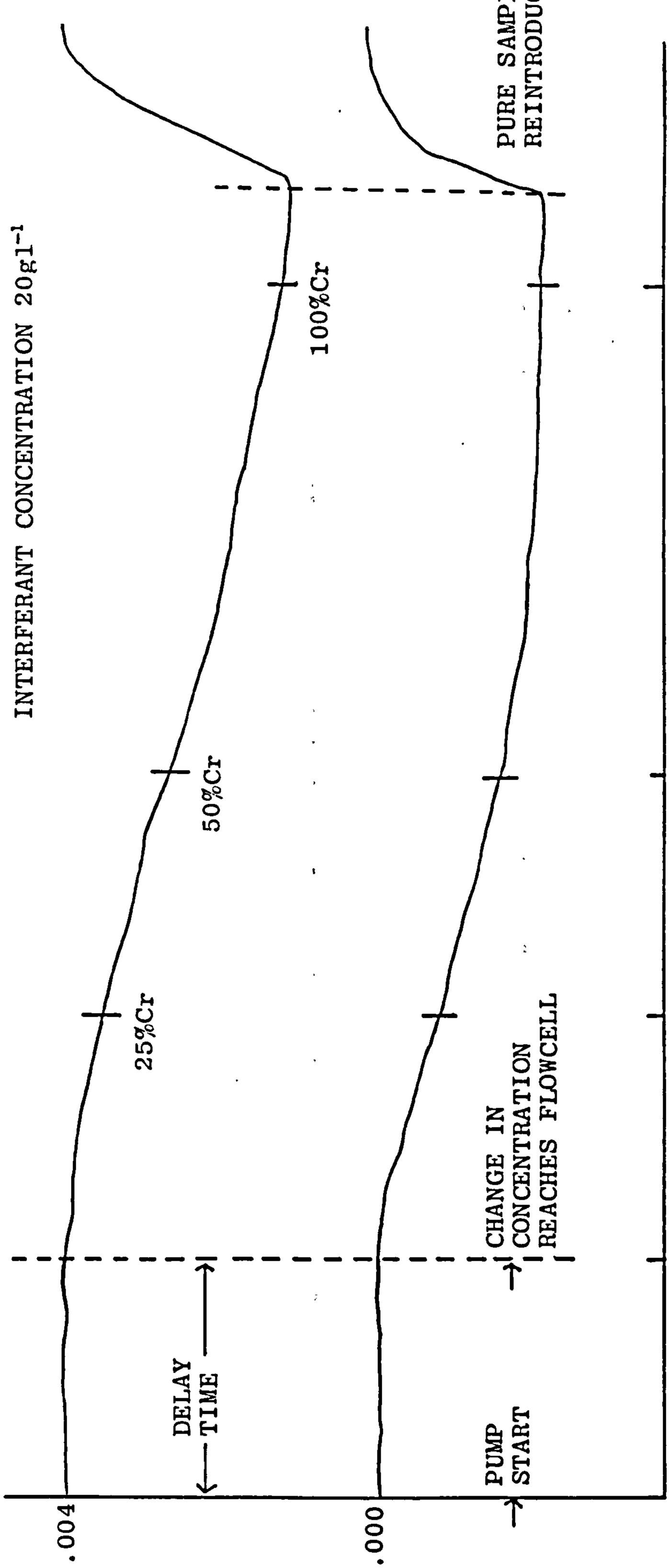


FIGURE 2.34 AUTOMATED FLUORIMETRIC INVESTIGATION OF INTERFERENCES CONTROLLED CONCENTRATION GRADIENT - CHROMIUM
INTERFERANT CONCENTRATION 20gl⁻¹
100%Cr
50%Cr
25%Cr
PURE SAMPLE REINTRODUCED
CHANGE IN CONCENTRATION REACHES FLOWCELL
DELAY TIME
PUMP START
TIME ⟶
t½
t¼
t⅛
t₀
.004
.000
RECORDER SCALE (%B)

FIGURE 2.35 THORON - AUTOMATED METHOD EFFECT OF VARIOUS METALS

INTERFERANT	AMOUNT OF ADDITION (EQUIV. % IN STEEL)	CHANGE IN READING (%B)	
		0.004%B	BLANK SOLN.
IRON	100	-.0001	-
CHROMIUM	50	-.0015	-.0012
	20	-.0005	-.0004
	10	-.0001	-.0002
	5	<.00005	<.00005
NICKEL	50	-.0001	<.00005
	20	-.00005	"
	10	<.00005	"
COBALT	40	-.0003	<.00005
	20	-.0001	"
	10	<.00005	"
MANGANESE	20	+.0002	<.00005
	10	+.0001	"
	5	<.00005	"
TITANIUM	7.5	-.0003	-.0003
	5	-.0001	-.0001
	2	<.00005	<.00005
MOLYBDENUM	10	+.0001	-
VANADIUM	30	<.00005	-
COPPER	50	<.00005	-

0.004% BORON IS $0.4 mgl^{-1}$ IN SAMPLE SOLUTION

10% INTERFERANT IS $1 gl^{-1}$ IN SAMPLE SOLUTION

2.7 Discussion - Fluorescence determination of boron in steel

This portion of the investigation has shown that thoron (4(2'-arsenophenylazo)-3-hydroxynaphthalene-2,7-disulphonic acid), which had been previously reported by Marcanonatos et al to give fluorescence with boron, is a suitable reagent for the rapid and sensitive fluorimetric determination of boron in steel.

The use of thoron allows the direct determination of boron in mild and low alloy steels, with no requirement for separation of other constituents. The fluorescent complex forms at ambient temperature in contrast to one of the most widely studied fluorimetric reagents for boron, HCMB, which while slightly more sensitive, requires heating to develop maximum fluorescence.

The certification work on a BCS stainless steel exemplifies that extension of the use of the proposed procedure to highly alloyed steels can be made without loss of accuracy if the matrices of samples and standards are matched. Even using this more involved calibration procedure, the method retained an advantage in speed and simplicity over methods requiring matrix removal before the final determination (for example the British Standard colorimetric method).

With the flowcell constructed for the automated procedure the illuminated area corresponded more closely to the cell dimensions than the 1cm cell used in the manual procedure. The effect of changes in solution transmission were decreased and the small effect of iron on the fluorescence output was further reduced, it may thus be possible,using such a cell, to

calibrate with sufficient accuracy using pure boric acid solutions.

A simple filter fluorimeter is suitable for the measurement of the fluorescence of the boric acid - thoron complex as the Stokes' shift is over 150 nm. This enhances the method's acceptibility as spectrofluorimeters are not widely available in the steel industry. An adaption of a simple filter absorptiometer by the addition of a suitable light source at right angles to the original source of illumination could,if necessary, provide a low cost instrument which would possess high sensitivity derived from broad band wavelength selection. An atomic absorption spectrophotometer, an instrument present in most if not all steel industry laboratories,should be similarly convertable into a filter - monochromator fluorimeter if used in the emission mode.

The established techniques for the dissolution of the steel sample are compatible with the fluorimetric method and acid soluble and insoluble boron may be determined separately if desired using the same procedure for development of fluorescence. With ICP the solvent of preference for the determination of boron in ferrous samples is a mixture of hydrochloric and nitric acids. This introduces practical difficulties in separating soluble and insoluble portions and their proportions may well be different from dissolution in sulphuric acid.

The investigation of other arsenophenylazo compounds has shown that arsenazos I and III give fluorescent complexes with boron in similar conditions to that of thoron. These have not

previously been reported.

The fluorescent complexes of boron and various arsenophyenylazonaphthalene derivatives were all formed in sulphuric acid (90% v/v) as is the case with the majority of the established colorimetric methods. It would be more convenient to be able to work in a more dilute acid medium. An investigation of the composition and stability of the boron complex in solution forms the next portion of this work in an attempt to establish if the complex is of the same type as those formed by reagents giving coloured complexes with boric acid in concentrated sulphuric acid and to assess the role of sulphuric acid in the complex formation mechamism.

3. DETERMINATION OF FORMULA AND STABILITY CONSTANT OF THORON-BORIC ACID COMPLEX

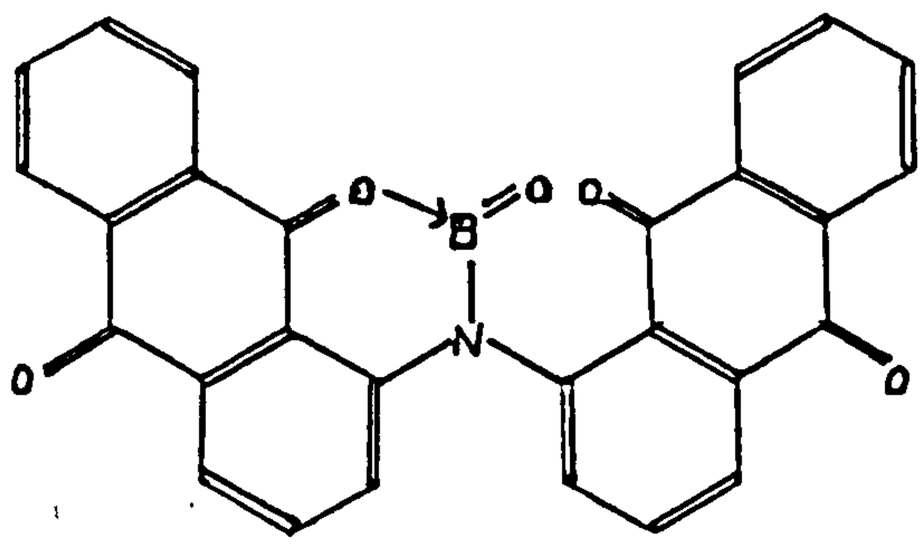
Limited information is available on the complex formation taking place with the various reagents that react with boric acid in strong sulphuric acid media. The systems for which most data are available are the analytically useful colorimetric reagents 1,1'dianthrimide (56,58), diaminochrysazin (59), quinalizarin (60,61) and carminic acid (62) and the fluorimetric reagent HCMB (2-hydroxy-4-methoxy-4'-chlorobenzophenone) (63,64). All these have been studied at equilibrium and the composition and apparent stability constants have been determined. The results are summarized in the table (Figure 3.1). In solution, 1:1 complexes predominate with apparent stability constants in the range 10^3 to $10^5 M^{-1}$.

Some workers have put forward possible structures for the boric acid complex. Langmyhr et al.(57,58) suggested formula I (Figure 3.2) for the complex with 1,1'dianthrimide when in solution and formula II for the isolated complex. In both of these proposed structures the boron atoms have a trigonal arrangement. For the complex between boric acid and quinalizarin Langmyhr and Holm (60) proposed the reaction scheme III. Marcantonatos and Menzinger (64) concluded that the HCMB complex was probably of the form IV and as in the previous scheme the complex contains a tetrahedral boron structure formed from $B(HSO_4)_4^-$.

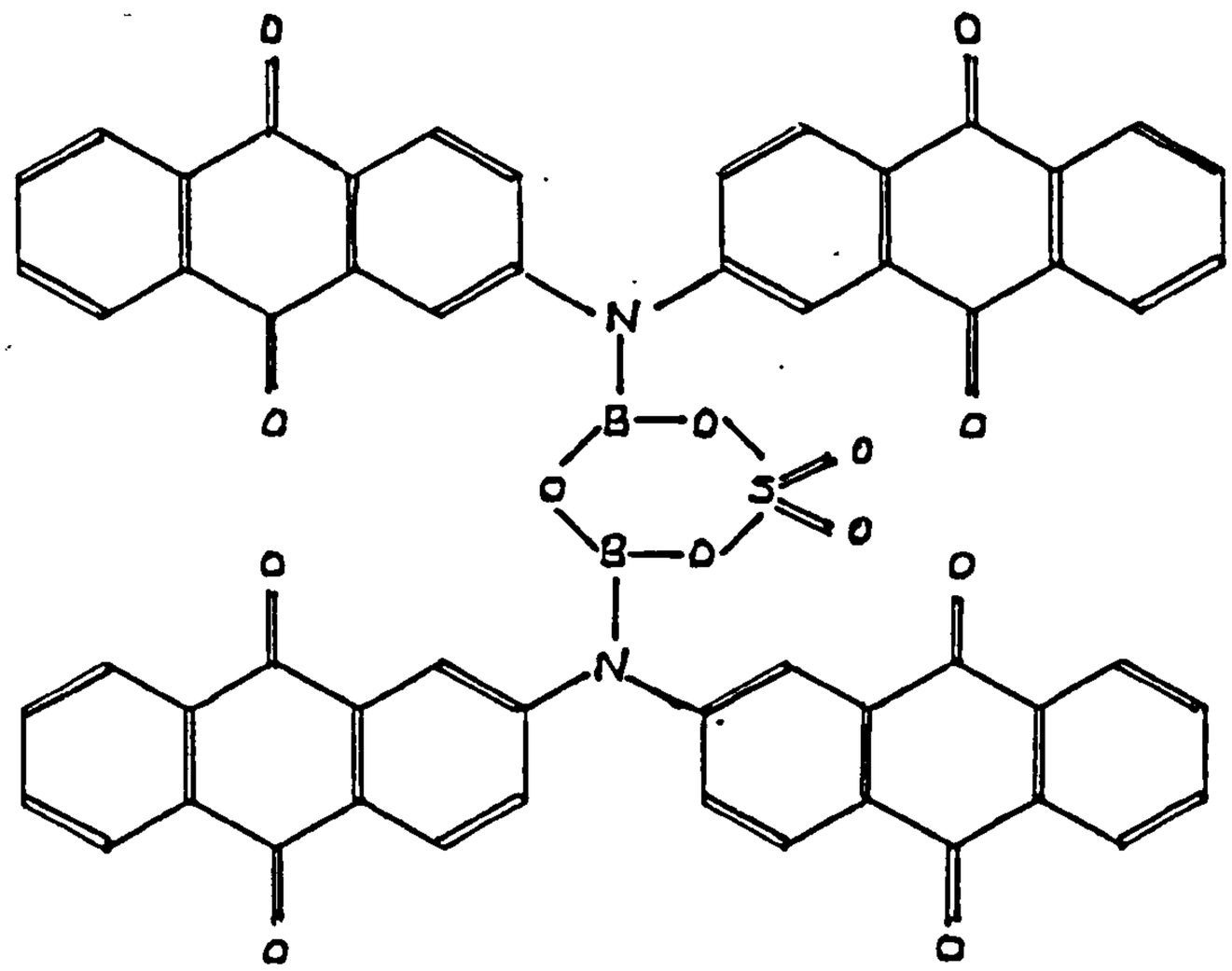
As no previous work had been done on the complex formation between thoron and boric acid under the conditions used for the proposed fluorimetric determination of boron in

FIGURE 3.1 SUMMARY OF FORMULA AND STABILITY CONSTANTS OF BORON COMPLEXES IN SULPHURIC ACID

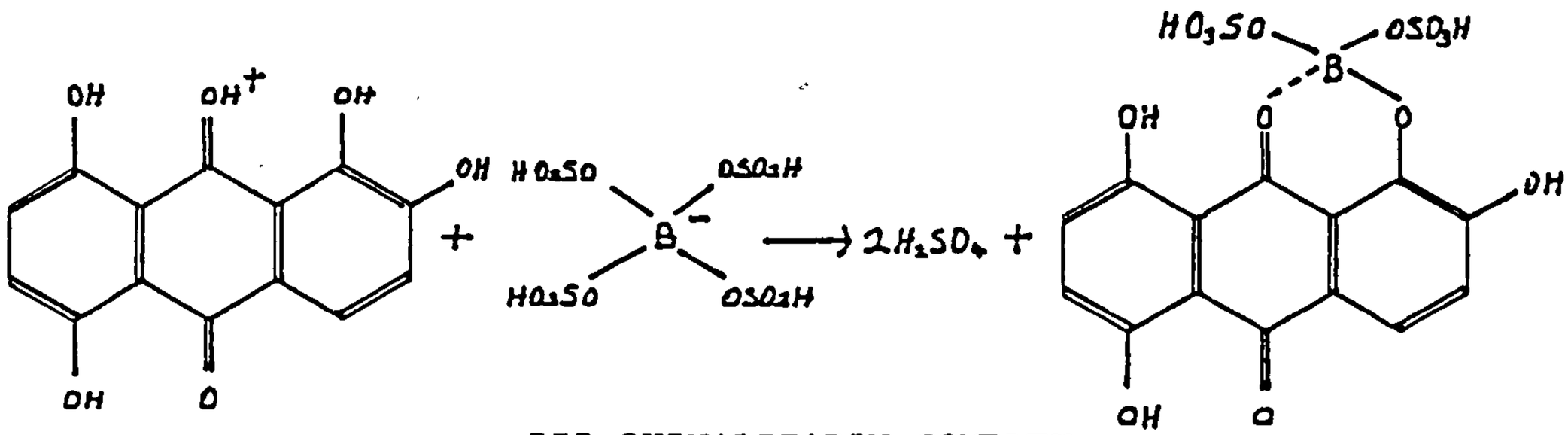
REAGENT	CONDITIONS	BORIC ACID:REAGENT	STABILITY CONSTANT β	REFERENCE
1,1'-DIANTHRIMIDE	90% w/w H_2SO_4 70°C FOR 48HR 2×10^{-4}M REAGENT + BORIC ACID	1:1	-	56
	94% H_2SO_4 70°C FOR 16HR 1×10^{-5}M	1:1	$1.4 \times 10^5 M^{-1}$	57
	ISOLATED COMPLEX	2:2	-	58
DIAMINOCHRYSAZIN	96% H_2SO_4 25°C 10^{-4} to 2×10^{-3}M	1:1	$3.5 \times 10^3 M^{-1}$	59
QUINALIZARIN	93% H_2SO_4 ROOM TEMP 15MIN 0.8×10^{-4}M	1:1	$8.7 \times 10^4 M^{-1}$	60,61
CARMINIC ACID	93% H_2SO_4 25°C 10^{-4}M	1:1	$1.9 \times 10^4 M^{-1}$	62
HCMB (2-HYDROXY-4-METHOXY-4'-CHLOROBENZOPHENONE)	96% H_2SO_4 70°C 4×10^{-6}M	1:1	$5 \times 10^4 M^{-1}$	63
	94 to 98% H_2SO_4 40°C 4×10^{-7}M	1:1	2 to $3 \times 10^4 M^{-1}$	64



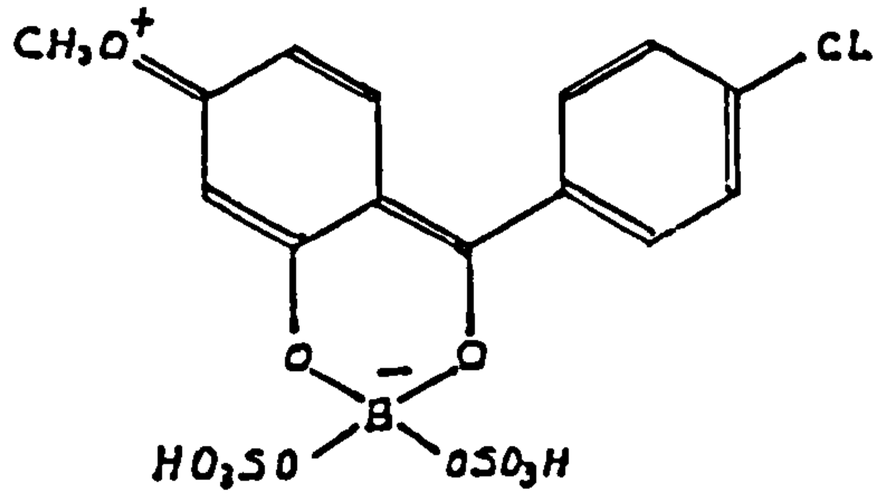
I 1,1'DIANTHRIMIDE COMPLEX



II 1,1'DIANTHRIMIDE COMPLEX - SOLID



III QUINALIZARIN COMPLEX



IV HCMB COMPLEX

FIGURE 3.2 SOME PROPOSED STRUCTURES OF BORIC ACID COMPLEXES

steel this portion of the investigation was undertaken to provide information on the formula and stability constant in strong sulphuric acid solution, determined from fluorimetric data.

3.1 Methods for the identification of the formula of the complex in solution

(a) The principle of continuous variations.

This is a simple technique and its limitations have been well documented. The method is attributed to Job (65) who applied it to complex systems, although the first use was many years earlier (66).

If the complex formation is represented by

$$mA + nB \rightleftarrows A_mB_n$$

a series of solutions is prepared in which the total concentration of A and B is constant,C, while the ratio between the reactants is varied.

$$[A_{initial}] + [B_{initial}] = C$$

If x is the amount of B present initially

$$[A] = (1-x)C - m[A_mB_n]$$

$$[B] = xC - n[A_mB_n]$$

$$[A_mB_n] = \beta[A]^m[B]^n$$ where β is the cumulative formation constant.

When the concentration of the complex reaches a maximum the value of x is obtained by setting $d[A_mB_n]/dx = 0$ after differentiating the above equations

$$m(Cx - n[A_mB_n]) = n((1-x)C - m[A_mB_n])$$

$$m\,x_{max} = n(1-x_{max})$$

$$\frac{n}{m} = \frac{x_{max}}{1-x_{max}}$$

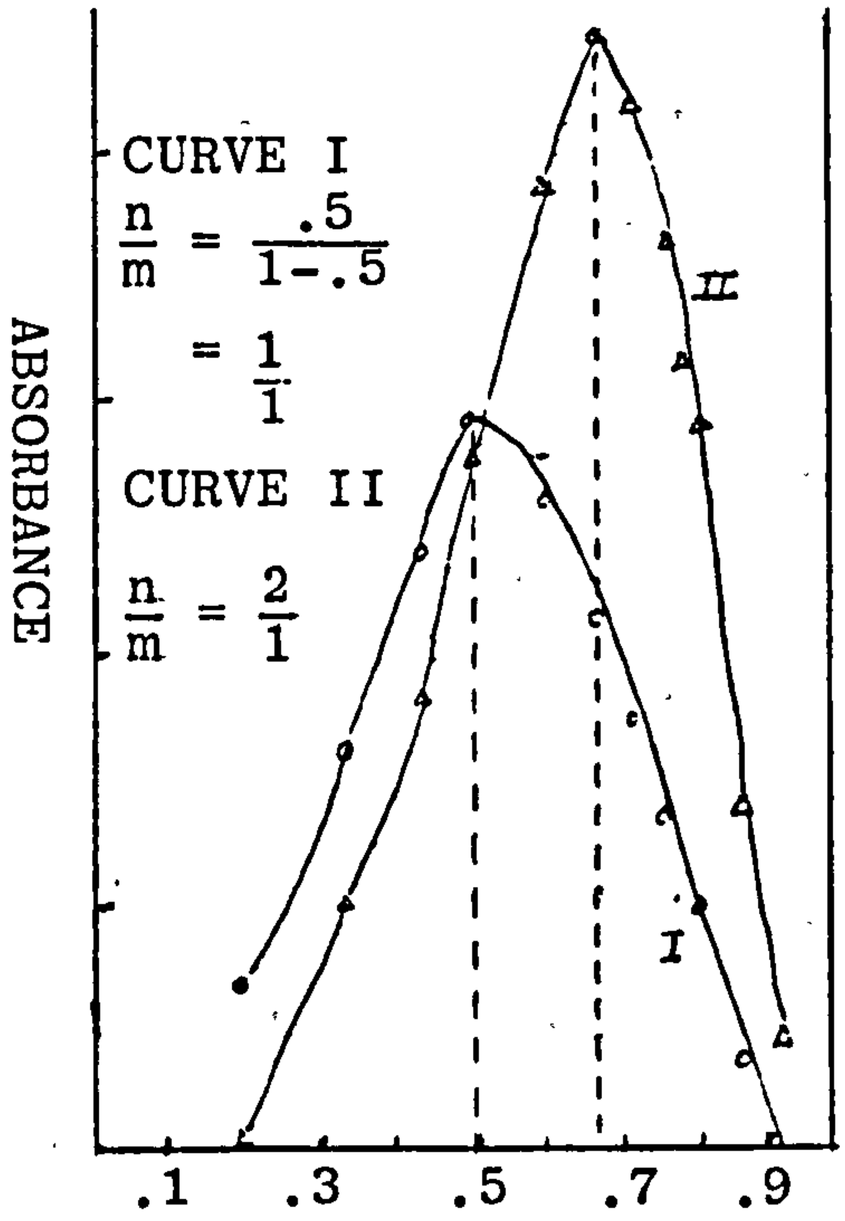
The ratio n/m can be obtained by plotting any property of the solutions which varies linearly with the concentration of the complex, usually but not necessarily spectrophotometric data, as a function of the mole fraction of B. (Figure 3.3a).

Klausen and Langmyhr (67) have shown that for $n = m > 1$ the curve may exhibit inflections and parabolic portions near $x = 0$ and 1 but not if $n = m = 1$. The procedure is not suitable for complexes where $n/m > 3$ as a small error in x_{max} will result in an incorrect ratio.

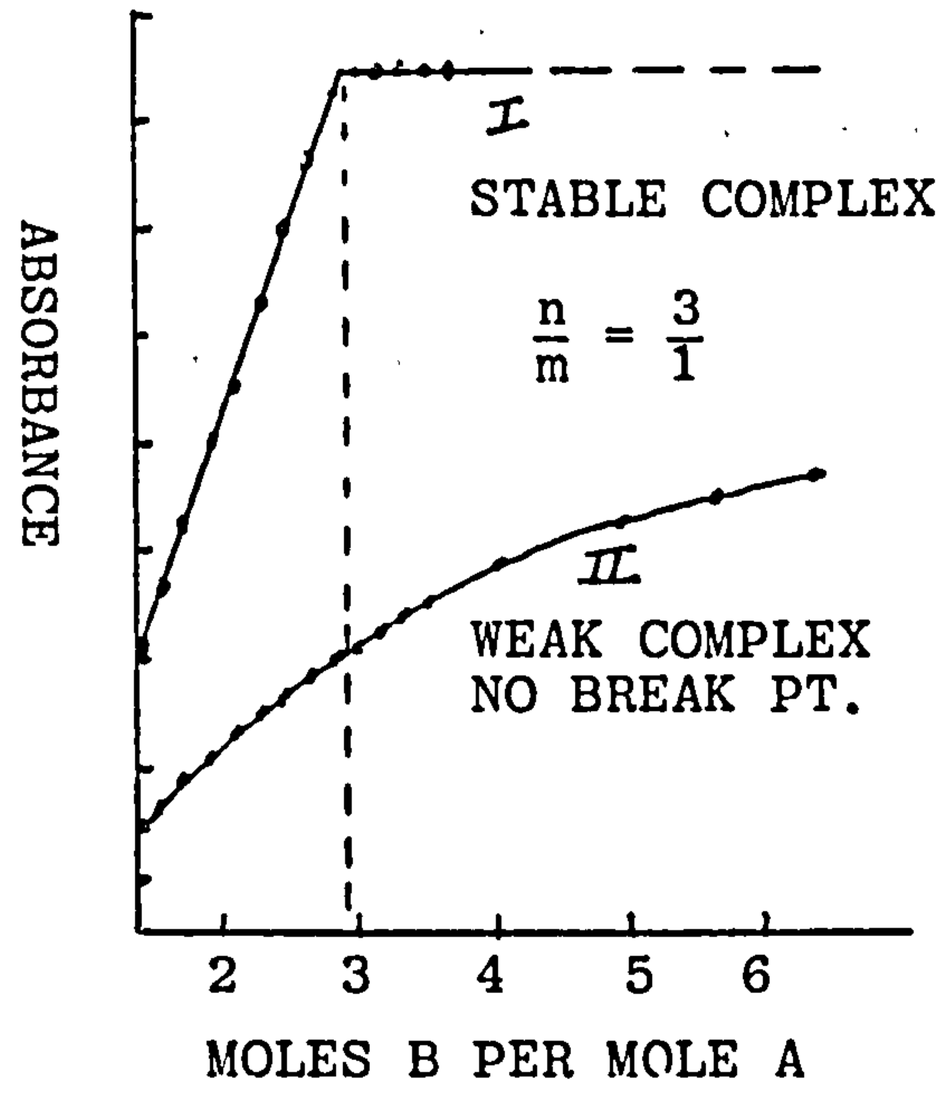
Measurements should be made at a constant, high ionic strength to eliminate changes of activity coefficients with changes in concentration. If more than one complex is formed unreliable results may be obtained.

Vosburgh and Cooper (68) extended the applicability of the technique by making a series of absorption measurements at a variety of wavelengths. If only one compound is formed the results are independent of the wavelength used. When more than one compound is formed the results depend on the wavelength used unless all but one do not absorb. The modification of Vosburgh and Cooper has been extended by Freeman and White (69) who used both fluorescence and absorbance measurements on the same complex, and to fluorescence measurements (51) where similar considerations apply.

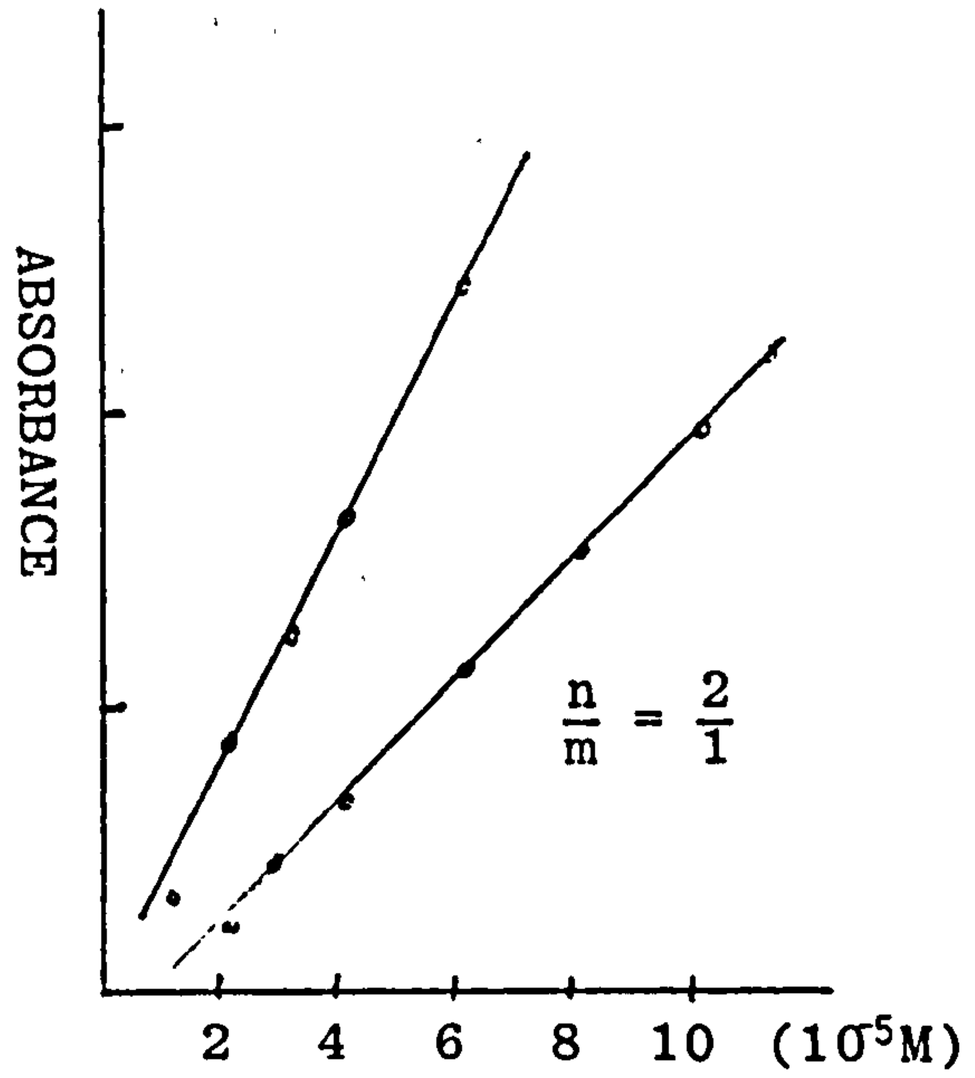
FIGURE 3.3 METHODS FOR DETERMINATION OF FORMULA OF COMPLEX



a) CONTINUOUS VARIATION METHOD EX REF 71



b) MOLE RATIO METHOD YOE AND JONES REF 70



c) SLOPE RATIO METHOD HARVEY AND MANNING REF 71

(b) Mole ratio methods

As in the preceding section if the complex formation

$$mA + nB \rightleftarrows A_mB_n$$

is considered, Yoe and Jones (70) have shown that when the total concentration of A is kept constant while the total concentration of B is increased, if only one complex of high stability is formed, a plot of a linear spectroscopic property of the complex (again usually absorbance) as a function of total concentration of B consists of two linear parts. At their intersection the ratio of concentrations of B and A gives the ratio n : m directly. The position of the break becomes increasingly uncertain with complexes of lower stability until a smooth curve is obtained on increasing the amount of B and no reliable information can be obtained. (Figure 3.3b).

Harvey and Manning (71) proposed a modification in which A or B is kept in constant excess while the other component is varied. The ratio of the slope of the linearly variable spectroscopic property versus the concentration of the variable component establishes the ratio n : m. (Figure 3.3c). For complexes of low stability the method of Bent and French (72) allows not only the ratio n : m but values of the coefficients to be obtained.

$$\log[A_mB_n] = m\log[A] + n\log[B] + \log\beta$$

For a weak complex [A] is approximately $[A_{initial}]$ and similarly for B. $[A_mB_n]$ is proportional to the linearly variable spectroscopic property, I, so that log I plotted as a function of [B] at constant large [A] gives a straight line of slope n. A similar procedure with B in excess leads to a value for m.

If the ratio obtained experimentally is unity it is necessary to know the approximate stability constant of the complex to be certain that the approximations are valid. Other methods have been proposed such as the method of Asmus (73) modified by Holme and Langmyhr (61) which gives a straight line for the correct quotient of n : m for a plot of $^{1}/_{[B]^{n}}$ against $^{1}/_{I}$.

The stability of the boric acid - thoron complex is not known but the stability constants which have been published for coloured boric acid complexes in strong sulphuric acid show that they are of moderate stability. The method of continuous variation was chosen for the investigation of the thoron complex as the mole ratio methods give uncertain results with complexes of low stability (Yoe and Jones) or are based on the assumption of complete dissociation (Bent and French). The Vosburg and Cooper modification of the method was used for the experimental work. It was thought unlikely that the limitations of the method would be detremental to its successful application. The strong sulphuric acid medium would provide a constant ionic strength and the fluorescence had previously been shown to vary linearly with boric acid concentration.

3.2 Experimental identification of formula

A series of solutions in sulphuric acid (90% v/v) was prepared in which according to the principle of continuous variation,

$$[\text{Thoron}] + [\text{Boric acid}] = 10^{-5}\text{M}$$

and the boric acid mole fraction, x, varied from 0.1 to 1 as its concentration varied from 10^{-6}M to 10^{-5}M (approximately 0.01 to 0.1mgl^{-1} boron).

The fluorescence measurements were taken using instrumental conditions previously established. A thermostatted cell holder was used set at 25°C.

The graphs (Figure 3.4) show the variation of fluorescence intensity at 580 nm using differing excitation wavelengths after the complex had developed at room temperature for 36 hours and after heating at 90°C for 1 hour.

The maximum fluorescence intensity was observed at a value of

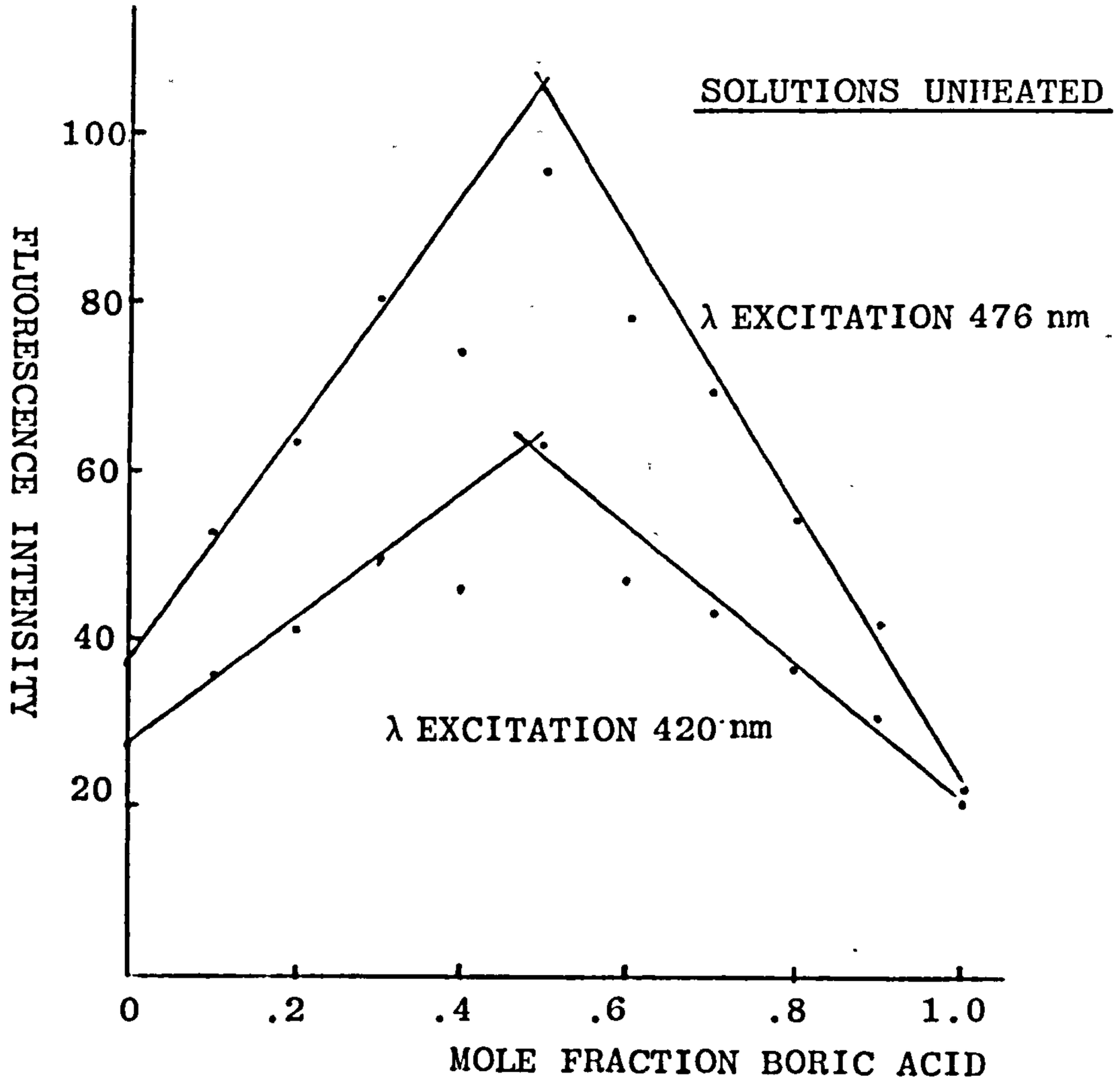
$$x\,max = 1/\left(1 + \frac{[Thoron]}{[H_3BO_3]}\right) = 0.5$$

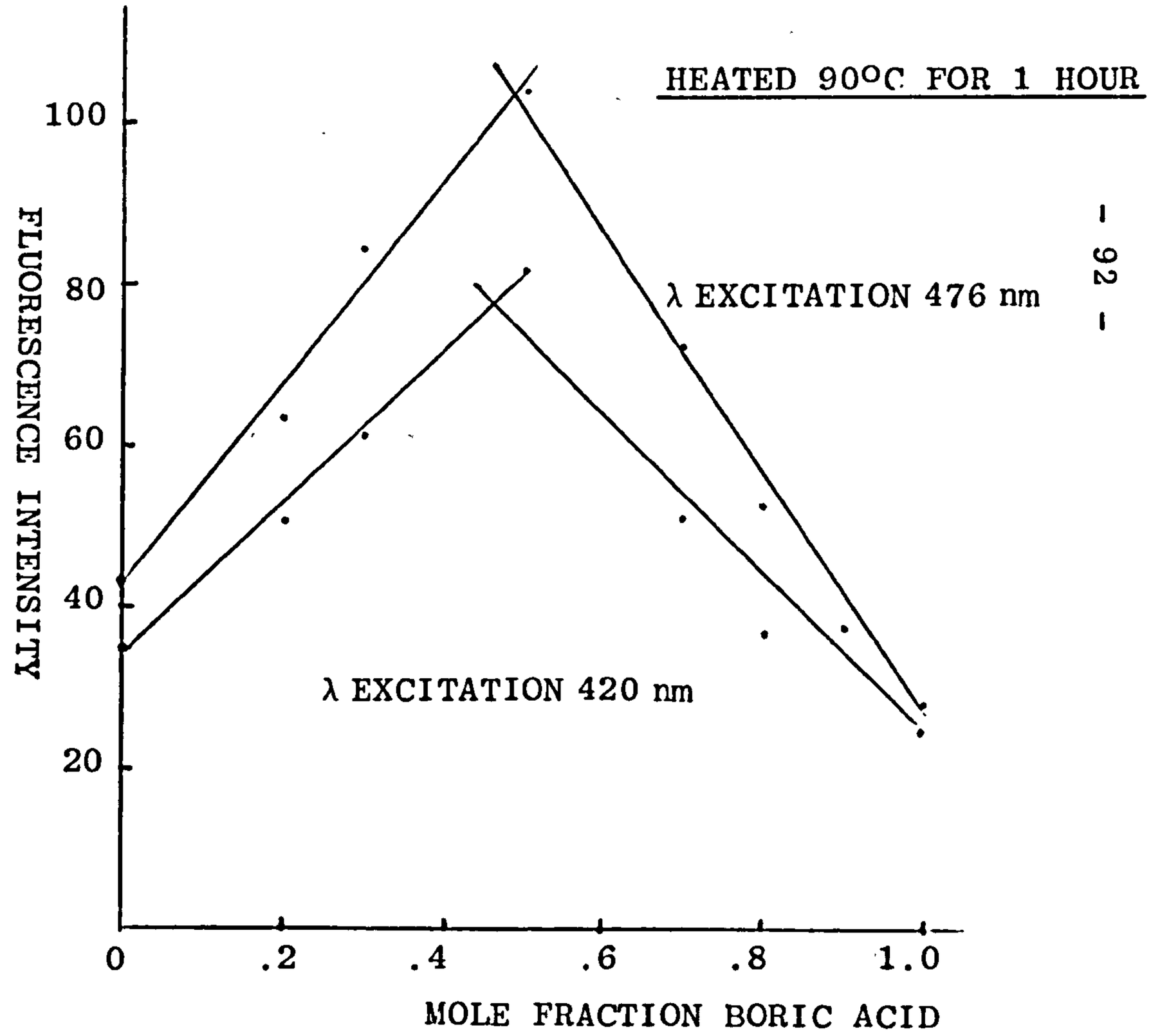
$$\therefore \quad [Thoron] = [H_3BO_3] = 5 \times 10^{-6}M$$

The graphs were linear at values of x near 0 and 1 and similar values of x_{max} were observed at all excitation wavelengths. This suggests that a single complex is formed containing one molecule of thoron combined with one molecule of boric acid. The existence of a 1 : 1 boric acid - thoron complex is supported by the results obtained in the investigation of calibration linearity detailed in section 2.2.2. The variation of fluorescence with increasing boric acid concentration (0 to 7×10^{-4}M) while the thoron concentration was held constant (1.44×10^{-4}M) was illustrated graphically in figure 2.5 and may be interpreted in the terms of the mole ratio procedure of Yoe and Jones. The

FIGURE 3.4 VARIATION OF FLUORESCENCE WITH VARIATION OF THORON AND BORIC ACID CONCENTRATION.

$[THORON] + [H_3BO_3] = 10^{-5}$





graph does not show a well defined break point but the linear portions when extended intersect at a boric acid concentration of 1.5×10^{-4}M. This corresponds to the formation of a complex with a ratio of concentrations of boric acid and thoron of 1.0.

These results are at variance with the work of Marcantonatos et al (51) who concluded that one molecule of thoron complexed with two of boric acid in concentrated sulphuric acid at a constant reactant concentration of 5×10^{-3}M but is consistant with other formulae which have been obtained for boron complexes in strong sulphuric acid.

3.3 Methods for the determination of stability constant

For a system where only one complex is formed

$$A + B \rightleftarrows AB$$

the apparent stability constant β_1 is given by

$$\beta_1 = \frac{[AB]}{[A][B]}$$ where [A],[B] and [AB] are equilibrium concentrations

or

$$= \frac{[AB]}{(A_o-[AB])(B_o-[AB])}$$

where A_o and B_o are initial concentrations and are known.

The formation of the complex can be followed by measurements of a property of the solution which varies linearly with its concentration. Spectrophotometric measurements of the absorbance,A, of coloured complexes enables the concentration of the complex to be derived from

$A = \varepsilon cd$ where ε is the molar absorptivity, c the concentration and d the path length

giving $[AB] = \frac{A}{\varepsilon_{AB} d}$

Molar absorptivity cannot always be directly determined. Similarly fluorescence measurements are related to complex concentration by

$I_f = I_o \phi \varepsilon c l$ where $I_f, I_o, \phi, \varepsilon, c$ and l are as defined in section 2.1

so that $[AB] = \frac{I_f}{I_o \phi \varepsilon l}$

or $= \frac{I_f}{k_f}$ if k_f is an overall constant.

The overall constant, k_f, contains contributions due to the fluorescent species itself and to instrumental factors and is found from measurements on the system being investigated.

Methods for the calculation of the stability constant from absorbance data which require independent determination of the molar absorptivity cannot be adapted to fluorescence measurements.

In the method of Holmes and Langmyhr (61)

$$[AB] = \frac{A}{\varepsilon d}$$

or more generally $[AB] = \frac{I}{k}$ where I is a linearly variable spectroscopic property and k is a constant.

so that $$\beta_1 = \frac{\frac{I}{k}}{\left(A_o - \frac{I}{k}\right)\left(B_o - \frac{I}{k}\right)}$$

if A_o is held constant and the concentration of B_o is increased the concentration of the complex approaches a maximum value when virtually all of A originally present, A_o, is complexed and I reaches a maximum value I_{max}.

Hence $$AB \simeq A_o = \frac{I_{max}}{k}$$

$$\beta_1 = \frac{A_o \frac{I}{I_{max}}}{\left(A_o - \frac{I}{I_{max}} \cdot A_o\right)\left(B_o - \frac{I}{I_{max}} \cdot A_o\right)}$$

The method of Rose and Drago (74) assigns a series of values to k and by use of the equation

$$\frac{1}{\beta_1} = \frac{I}{k} - A_o - B_o + \frac{A_o B_o k}{I}$$

the values of β_1 can be calculated. A series of plots of $\frac{1}{\beta_1}$ against k at different concentrations of A_o and B_o gives a series of straight lines which intersect at $\frac{1}{\beta_1}$.

For moderately stable complexes one of the reactants should be in a large excess to ensure the formation of a significant amount of the complex. Thus if one component is held constant and the other is in large excess and is varied

$A_o >> B_o$ B_o is constant

$$\beta_1 \simeq \frac{[AB]}{A_o(B_o-[AB])}$$

as before $[AB] = \frac{I}{k}$

$$\beta_1 \simeq \frac{\frac{I}{k}}{A_o(B_o-\frac{I}{k})}$$

$$\frac{1}{A_o} \simeq \beta_1\frac{k}{I}(B_o-\frac{I}{k})$$

$$\frac{1}{A_o} \simeq \beta_1\frac{k}{I}B_o - \beta_1$$

A plot of $\frac{1}{A_o}$ against $\frac{k}{I}B_o$ has a slope of β_1 and intercept $-\beta_1$.

This is a particular case of the equation first used by Stearns and Wheland (75) applicable when the measured property of the solution is independent of the concentration of A.

This procedure was chosen for the evaluation of the stability constant of the boric acid - thoron complex from fluorescence measurements.

For fluorescence the equation becomes

$$\frac{1}{A_o} \simeq \beta_1 \frac{k_f}{I_f} B_o - \beta_1$$

A plot of $\frac{1}{A_o}$ against $\frac{B_o}{I_f}$ gives a slope of $k_f\beta_1$, but still an intercept of $-\beta_1$ from which k_f can be calculated. If values of k_f close to that found graphically are substituted into the full equation

$$\beta_1 = \frac{\overline{k_f}}{\left(A_o - \frac{I_f}{k_f}\right)\left(B_o - \frac{I_f}{k_f}\right)}$$

β_1 can be recalculated and the value with minimum relative variability found.

3.4 Experimental determination of stability constant

Fluorescent solutions in sulphuric acid (90% v/v) were prepared so that the boric acid concentration was in large excess over a constant concentration of thoron. The thoron concentration, B_o, was 5×10^{-6}M, the boric acid concentration, A_o, was varied from 10^{-4} to 10^{-3}M (approximately 1 to 10mgl^{-1} boron).

The solutions were equilibriated at room temperature for two days and the fluorescent intensity was measured using a thermostatted cell at 25°C. The instrumental parameters used were those previously established.

The intensity values were corrected for the small blank fluorescence from a 5×10^{-6}M solution of thoron in sulphuric acid with no boric acid added. Boric acid blank solutions with no thoron gave negligible fluorescence. The data obtained are given in the tables (Figure 3.5). Two series of solutions were prepared the second having more equally spaced values for

FIGURE 3.5 DETERMINATION OF APPARENT STABILITY CONSTANT

THORON CONC. $B_o = 5 \times 10^{-6}$ M
BORIC ACID CONC. $A_o = 10^{-4}$ to 10^{-3} M
SULPHURIC ACID 90% v/v
TEMPERATURE 25°C
EXCITATION 476 nm

A_o /10^{-4}M	$\frac{A_o}{B_o}$	$\frac{1}{A_o}$ /$10^{3}M^{-1}$	FLUORESCENCE INTENSITY, I_f /CHART DIVS.	$\frac{B_o}{I_f}$ /10^{-8}M
SERIES I				
1	20	10	34.2	14.62
2	40	5	46.0	10.87
3	60	3.33	59.7	8.37
4	80	2.5	59.6	8.38
5	100	2	63.3	7.89
6	120	1.66	64.8	7.77
7	140	1.43	67.4	7.42
8	160	1.25	68.9	7.26
9	180	1.11	70.6	7.08
10	200	1.0	69.9	7.15
SERIES II				
1.0	20	10.0	40.3	12.41
1.1	22	9.09	41.7	11.99
1.25	25	8.0	45.0	11.11
1.4	28	7.14	47.6	10.50
1.7	34	5.88	52.5	9.52
2.0	40	5.00	57.3	8.72
2.2	44	4.55	59.0	8.47
2.5	50	4.0	62.8	7.96
2.85	57	3.51	64.1	7.80
3.3	66	3.03	67.3	7.43
4.0	80	2.50	70.2	7.12
5.0	100	2.0	74.6	6.70
6.25	125	1.6	78.8	6.35
8.3	166	1.20	82.2	6.08
10.0	200	1.0	85.4	5.85

FLUORESCENCE INTENSITY = PEAK HEIGHT CORRECTED FOR BLANK FLUORESCENCE

(ARBITRARY UNITS)

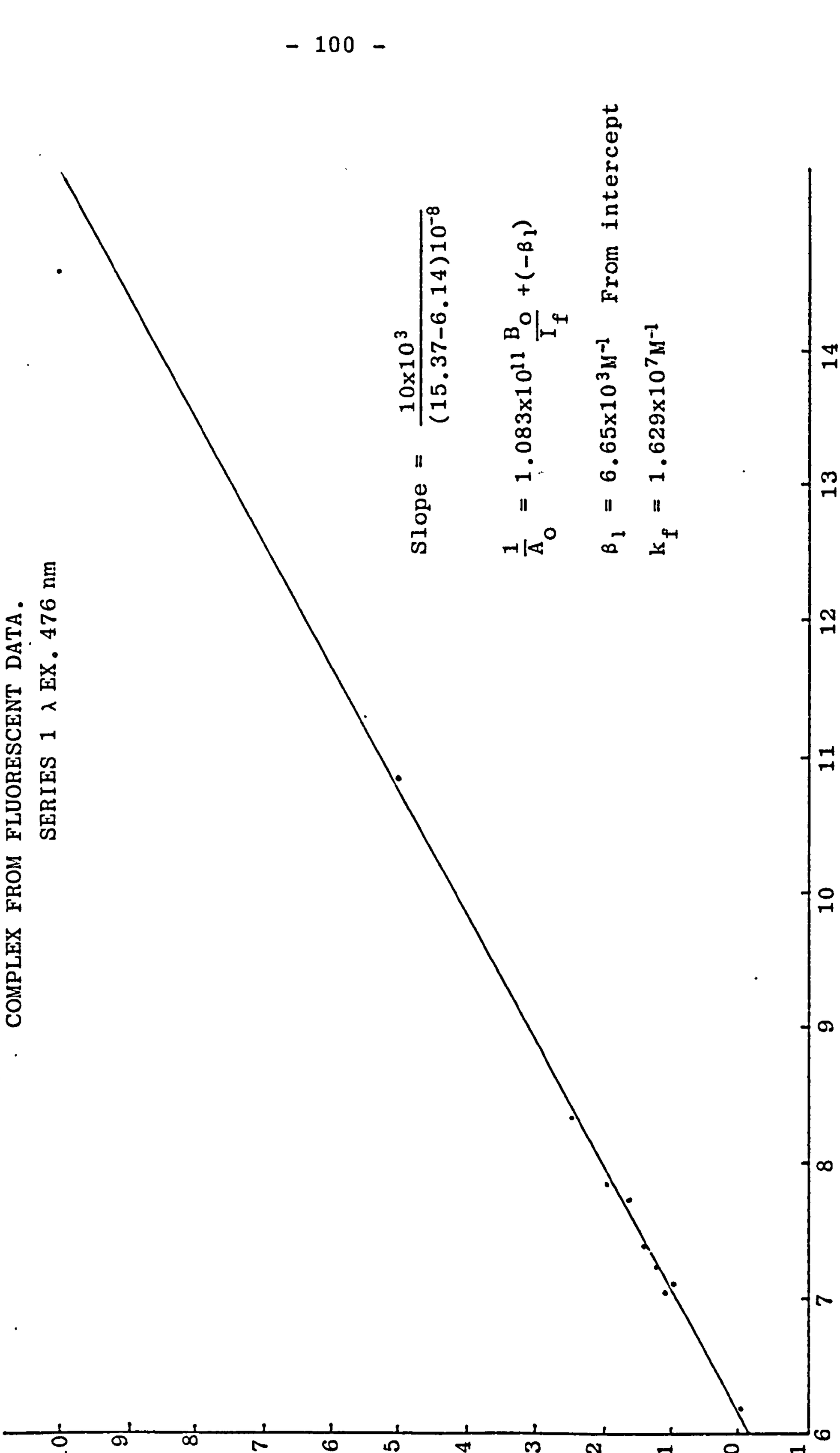
the reciprocal of the boric acid concentration and consequently a graphical determination of k_f less dependent on a few outlying points. The graphical determination of k_f is illustrated in the graphs. (Figures 3.6 and 3.7). Data for other excitation wavelengths are collected in appendix 3 and summarized in the table. (Figure 3.8).

The value of k_f obtained from the graph Figure 3.7 was used to recalculate the stability constant employing the full equation. Values close to the graphical value of k_f were also úsed. (see Figure 3.9). The standard deviation of the mean stability constants obtained from these values was in all cases higher than that obtained from the use of the graphically derived value of k_f based on an initial assumption that the concentration of boric acid A_o is in great excess. The values of the apparent stability constant β_1 calculated from the full equation, using graphically determined values of k_f, are given in Figure 3.10 for both series of measurements and for a range of excitation wavelengths.

The two series of measurements give mean values of stability constant which are in good agreement and the overall mean value of $7.0 \times 10^3\ M^{-1}$ is similar to that obtained from previous studies of 1 : 1 complexes of boric acid in strong sulphuric acid (10^3 to $10^5 M^{-1}$ - Figure 3.1).

FIGURE 3.6 DETERMINATION OF STABILITY CONSTANT OF THORON - BORIC ACID COMPLEX FROM FLUORESCENT DATA.

SERIES 1 λ EX. 476 nm



$$\text{Slope} = \frac{(10-0)\ 10^3}{(12.5-5.2)10^{-8}} = 1.37\times10^{11}M^{-2}$$

$$k_f\beta_1 = 1.370\times10^{11}$$

$$\beta_1 = 7.123\times10^3M^{-1}$$

$$k_f = 1.923\times10^7M^{-1}$$

FIGURE 3.7 DETERMINATION OF STABILITY CONTENT
SERIES II λ EXCITATION 476 NM

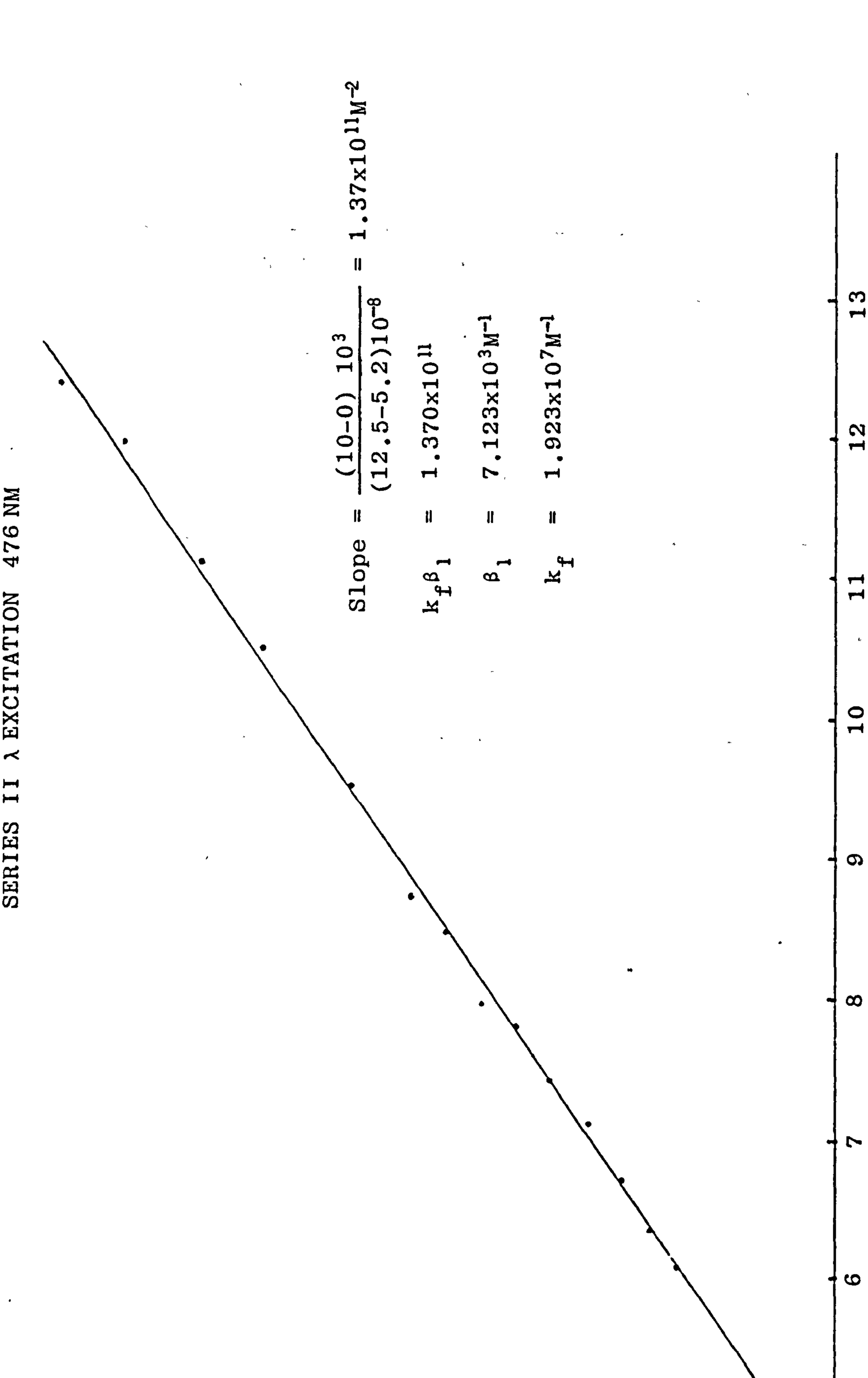


FIGURE 3.8 SUMMARY TABLE - DETERMINATION OF APPARENT STABILITY CONSTANT FROM FLUORESCENCE DATA

	EXCITATION WAVELENGTH /nm	$k_f\beta_1/M^{-2}$ FROM SLOPE	β_1/M^{-1} FROM INTERCEPT	k_f/M^{-1}
SERIES I	420	0.471×10^{11}	6.18×10^3	7.62×10^6
	476	1.083×10^{11}	6.65×10^3	1.63×10^7
	486	0.994×10^{11}	6.53×10^3	1.52×10^7
SERIES II	420	0.666×10^{11}	7.18×10^3	8.44×10^6
	476	1.370×10^{11}	7.12×10^3	1.92×10^7
	486	1.280×10^{11}	7.25×10^3	1.77×10^7

FIGURE 3.9 CALCULATION OF STABILITY CONSTANT - FULL EQUATION

SERIES II EXCITATION 476 nm

A_o /10^{-4}M	$\frac{A_o}{B_o}$	I_f /CHART DIVS	STABILITY CONSTANT $\beta_1/10^3M^{-1}$ AT VALUE OF $k_f/10^7M^{-1}$ OF					
			1.8	1.85	1.9	1.923*	1.95	2.0
1.0	20	40.3	8.29	7.89	7.53	7.37	7.20	6.89
1.1	22	41.7	8.02	7.62	7.26	7.10	6.93	6.63
1.25	25	45.0	8.16	7.73	7.34	7.17	6.99	6.66
1.4	28	47.6	8.17	7.71	7.30	7.13	5.90	6.60
1.7	34	52.5	8.38	7.85	7.39	7.19	6.97	6.60
2.0	40	57.3	8.90	8.27	7.72	7.48	7.23	6.81
2.2	44	59.0	8.78	8.12	7.55	7.32	7.07	6.63
2.5	50	62.8	9.27	8.58	7.90	7.63	7.34	6.84
2.85	57	64.1	8.79	8.02	7.37	7.10	6.81	6.34
3.3	66	67.3	9.09	8.18	7.44	7.15	6.82	6.30
4.0	80	70.2	8.95	7.95	7.14	6.83	6.49	5.94
5.0	100	74.6	9.75	8.40	7.37	6.97	6.57	5.92
6.25	125	78.8	11.34	9.26	7.83	7.32	6.79	5.98
8.3	166	82.2	12.78	9.66	7.77	7.14	6.50	5.59
10.0	200	85.4	18.62	12.07	8.94	7.98	7.08	5.87
		MEAN	9.83	8.49	7.59	7.26	6.85	6.37
		STANDARD DEVIATION	2.75	1.14	0.43	0.28	0.37	0.42

* VALUE OF k_f FOUND GRAPHICALLY

FIGURE 3.10 STABILITY CONSTANT CALCULATED FROM FULL EQUATION*

EXCITATION WAVELENGTH /nm	STABILITY CONSTANT/$10^3 M^{-1}$	
	SERIES I	SERIES II
486	6.66	7.40
476	6.79	7.26
420	6.30	7.34
MEAN	6.58	7.34

$$* \quad \beta_1 = \frac{[\text{COMPLEX}]}{[\text{BORIC ACID}][\text{THORON}]}$$

$$= \frac{AB}{(A_o - AB)(B_o - AB)}$$

$$= \frac{\frac{I_f}{k_f}}{\left(A_o - \frac{I_f}{k_f}\right)\left(B_o - \frac{I_f}{k_f}\right)}$$

3.5 Discussion

The experimentally determined stability constant allows the amount of boron combined as the thoron complex to be calculated. Under the conditions proposed for the analytical work in appendix 1 with a boric acid concentration 1.4×10^{-6}M and a thoron concentration 1.5×10^{-4}M, 51% of the boric acid was present as the chelate at equilibrium. It follows that a greater possibility exists for this equilibrium concentration to be significantly changed in either direction if experimental parameters such as temperature or reagent concentration were not kept constant than if the analyte was almost completely complexed.

Changes in fluorescence intensity caused by any temperature dependence of the equilibrium should not be noticeable in the proposed manual analytical procedure for the determination of boron in steel as the sample and standard solutions are at ambient temperature prior to measurement of their fluorescence. The fluorescence intensity obtained using the automated procedure, where measurements are made before the reaction has reached equilibrium, would be more dependent on changes in solution temperature during a series of analyses.

It would be expected that increasing the excess of thoron would increase the resultant fluorescence as the equilibrium is displaced in favour of complex formation. In section 2.4.2 the reverse was found to be the case but this can be explained by the increasing absorption of both exciting and fluorescence

radiation as the thoron concentration is increased, the inner filter effect. If the effects of increased absorption by the solution could be counteracted by frontal illumination of the sample, it may be possible to use a greater excess of thoron and so push the equilibrium further towards completion. A five fold increase in thoron concentration would increase the amount of boric acid complexed to 84% (Figure 3.11) but the use of the less common frontal illumination configuration, the increased reagent usage and associated solubility considerations would detract from the ease of application of the analytical procedure.

The apparent stability constant ($7 \times 10^3 M^{-1}$) is many magnitudes less than those of metallic complexes with thoron (β_1 for thorium complex $1.4 \times 10^{10} M^{-1}$ and for ruthenium and rhodium complexes($8 \times 10^8 M^{-1}$)(76,77))but is comparable with values obtained for other 1 : 1 complexes of boric acid in strong sulphuric acid media (10^3 to $10^5 M^{-1}$) especially as these values have been determined using differing acid concentrations and temperatures. The similar stability constants suggest that the boron atom has a similar environment in those complexes. There is however discrepancy about the form of the boron complexing species. As illustrated in the introduction to this chapter, early workers assigned a trigonal structure to the boron atom. (Figure 3.1I). Gillespie et al (78,79) in cryoscopic and conductiometric investigations of boric acid solutions in concentrated sulphuric acid proposed that in dilute boric acid solutions boron is present in the form of tetra

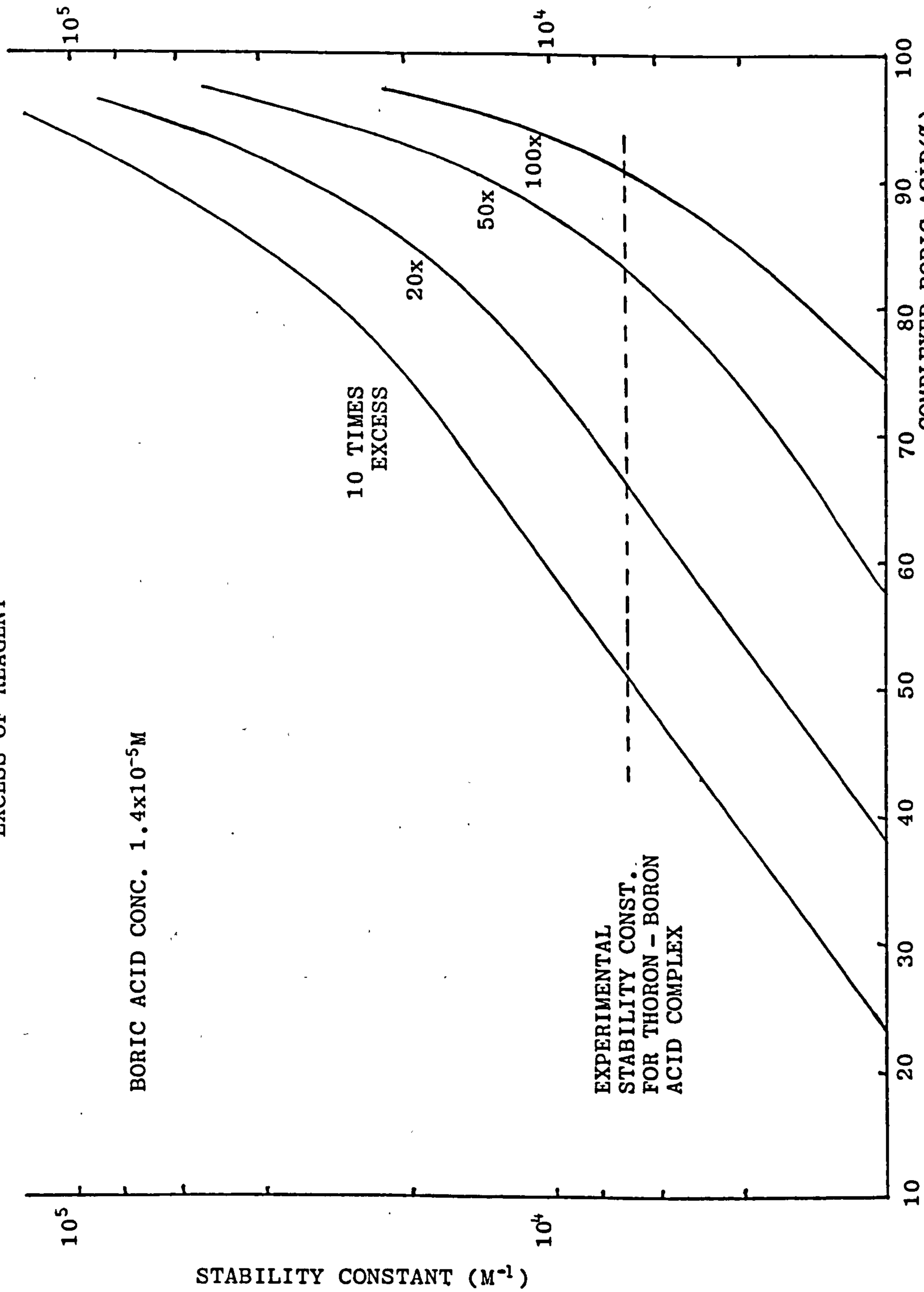


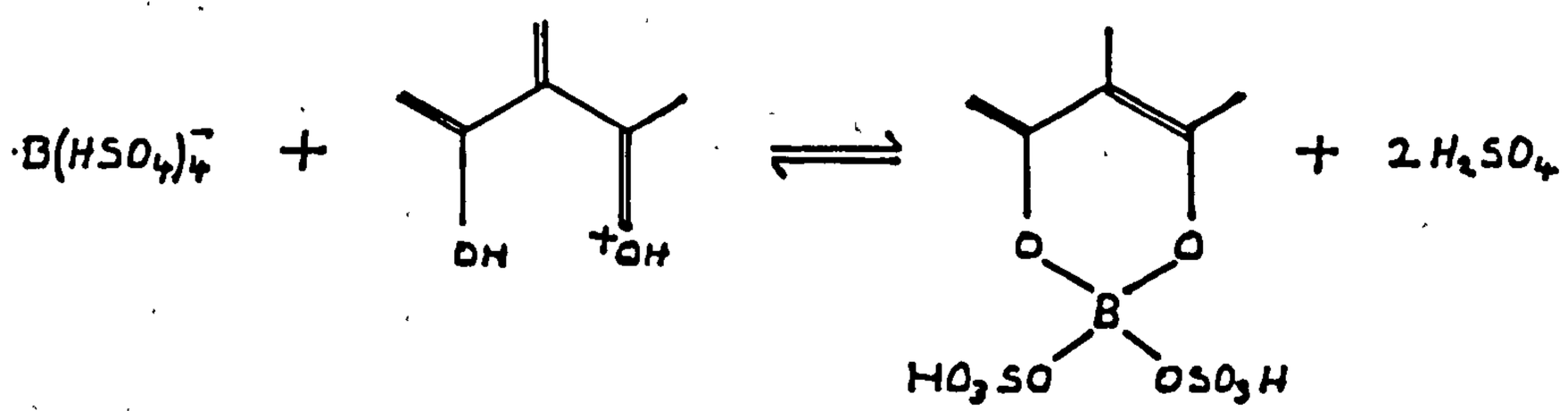
FIGURE 3.11 AMOUNT OF BORIC ACID COMPLEXED WITH VARIOUS EXCESS OF REAGENT

(hydrogensulphato) borate anions

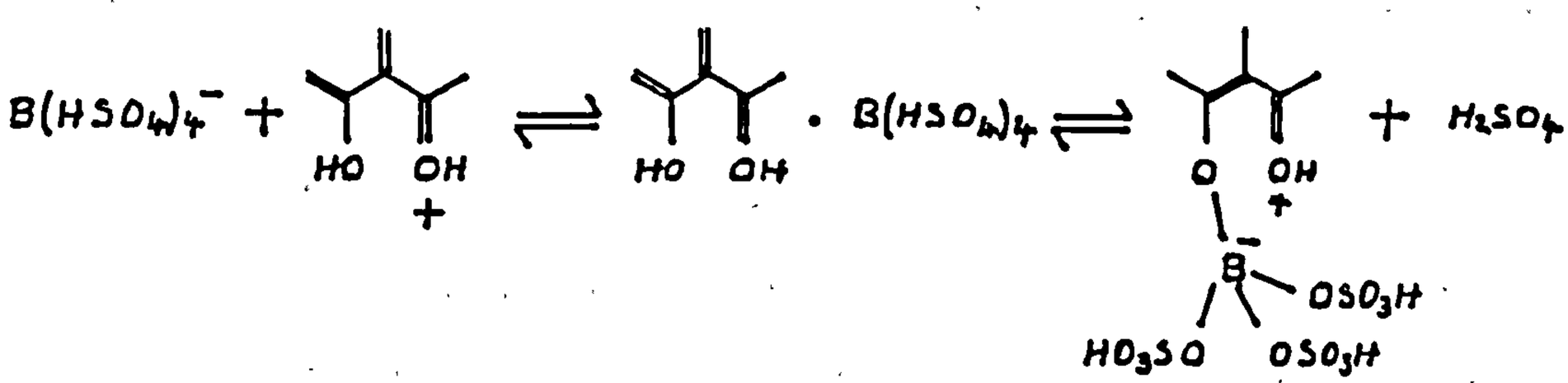
$$H_3BO_3 + 6H_2SO_4 \rightarrow B(HSO_4)_4^- + 3H_3O^+ + 2HSO_4^-$$

It seems more probable that the boron exists in tetrahedral configuration in complexes formed in concentrated sulphuric acid. The proposed structures of boron complexes put forward by Langmyhr and Marcantonatos (Figures 3.1 III and IV) are consistent with Gillespie's work.

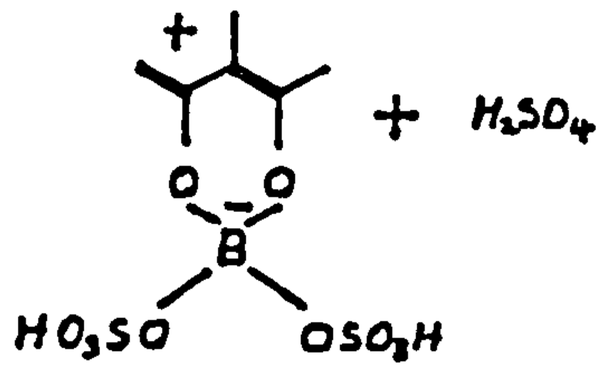
Marcantonatos et al (64) have also shown from kinetic studies that the simplest assumption for boric acid complex formation, a reversible reaction between tetra (hydrgensulphato) borate anion and protonated ligand (Figure 3.12 I) did not fully explain their results. A two step rate determining reversible reaction (Figure 3.12 II) gave closer agreement with their experimental work and they also postulated that boric acid may exist in the form $B(OH)(HSO_4)_3^-$ to explain the increase in overall rate constant with slight decreases in sulphuric acid concentration giving a reaction scheme (Figure 3.12 III) where the decrease in acid concentration produces a shift of equilibrium towards $B(OH)(HSO_4)_3^-$ and a highly favoured water displacement step. Similar variations in the rate of complex formation with variation of sulphuric acid concentration have been observed with 1,1'-dianthrimide and carminic acid adding more weight to the proposed existence of the $B(OH)(HSO_4)_3^-$ species.



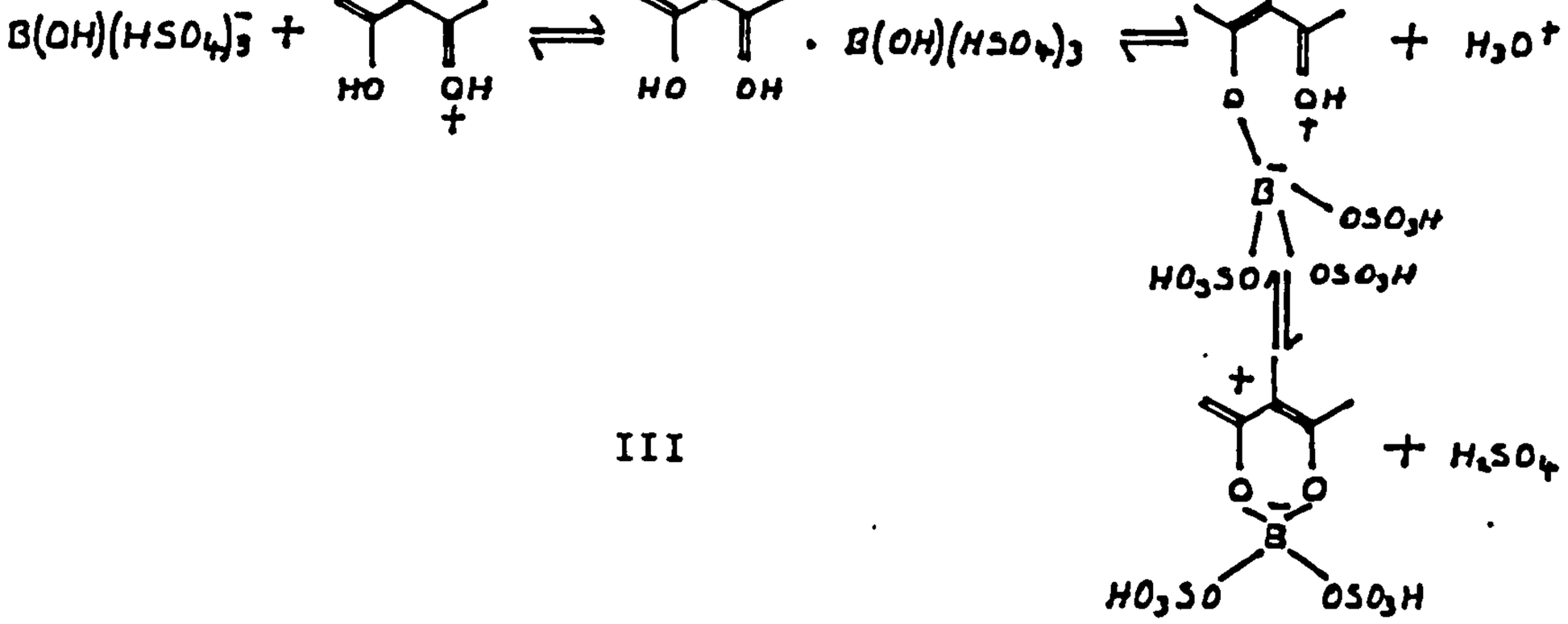
I



II



$$B(HSO_4)_4^- + H_3O^+ + HSO_4^- \rightleftharpoons B(OH)(HSO_4)_3^- + 2\,H_2SO_4$$



III

FIGURE 3.12 MECHAMISM OF BORON - HCMB COMPLEX FORMATION (64)

There appears to have been no further work on elucidating Marcantonatos' proposed reaction scheme. In order to obtain an insight into the thoron - boric acid system it is desirable to demonstrate the existence of the proposed borate anions in sulphuric acid media and also to confirm their configuration. It would seem that boron nuclear magnetic resonance spectroscopy studies might provide the necessary information and might also allow a comparison to be made of the configuration of the boron atom in the thoron and other boric acid complexes in conditions similar to that used for the analytical work. An independent estimate of apparent stability constants should also be possible. The potential of ^{11}B n.m.r spectroscopy as a means of further investigating the thoron - boric acid system is evaluated in the following chapter.

4. BORON NUCLEAR MAGNETIC RESONANCE STUDY OF BORIC ACID COMPLEXES IN SULPHURIC ACID

Potentiometric methods (80) have been widely used as a means of studying the equilibrium of boric acid, borate ions and complexing agents in aqueous solutions. Data on the structure and concentration of the complexes obtained by use of such procedures was mainly indirect. Spectroscopic methods provide means for directly measuring the concentration of species in solution. Ultraviolet (81) and Raman (82) spectroscopy have been used to study borate complex formation but it is only comparatively recently that extensive n.m.r. studies have been reported.

Both boron isotopes are n.m.r. sensitive. The table (Figure 4.1) gives some pertinent physical data of the isotopes.

FIGURE 4.1 PHYSICAL DATA FOR ^{10}B and ^{11}B NUCLEI.

NUCLEUS	^{10}B	^{11}B
SPIN NO.	3	$^{3}/_{2}$
RESONANCE FREQUENCY AT 1.9T(^{1}H 80MHz)	9MHz	26MHz
" " " 9.4T(^{1}H 400MHz)	42MHz	128MHz
NATURAL ABUNDANCE	18.8%	81.2%
RELATIVE SENSITIVITY AT CONSTANT FIELD FOR EQUAL NO.OF NUCLEI (^{1}H=1.00)	$1.9x10^{-2}$	0.16
RELATIVE SENSITIVITY 1M soln (^{1}H=1.00)	$3.5x10^{-3}$	0.12

The resolution of ^{11}B n.m.r. spectra is better than that of ^{10}B spectra as the resonance frequency is higher and the quadrupole moment is smaller giving greater line separation and narrower line width. The intrinsic sensitivity of ^{11}B is also about 40 times higher than ^{10}B.

Early workers (83,84) used ^{11}B n.m.r. spectroscopy to investigate the effect of boron concentration, pH and alkali metal ions on the equilibrium between boric acid, borate and polyborate species. In dilute solutions only one average signal was observed due to fast exchange (on the n.m.r. time scale) of boric acid and borate.

Henderson et al.(85) were the first to use ^{11}B n.m.r. for identifying borate esters of diols. They determined association constants of 1 : 1 and 1 : 2 complexes at pH12 by direct measurement of peak areas. Pasdeloup and Brisson (86) investigated the complexation of boric acid with catechol over a range of pH and concentration and also obtained ^{11}B resonances characteristic of 1:1 and 1 : 2 complexes. The pH dependence of the stability of esters of boric acid and borates was further investigated by Van Duin et al.(87) who found ^{11}B n.m.r. a suitable analytical tool for the quantitative determination and structure elucidation of esters in aqueous medium.

Henderson and Pasdeloup carried out their measurements at 29MHz while Van Duin et al.used a spectrometer operating at 64MHz.

No literature references to ^{11}B n.m.r. studies in very acid solutions were found. However, the work on borate esters of diols

illustrates that although the equilbria are rapidly established in aqueous solution, in contrast to the boric acid - borate system the reaction rates were sufficiently low for separate resonances to be observed and allowed the stability of the complexes to be calculated from peak areas of the n.m.r. spectra. This was sufficiently encouraging for an ^{11}B n.m.r. investigation of boric acid solutions in strong sulphuric acid to be made.

4.1 ^{11}B n.m.r. at 25.7MHz

The preliminary investigations were made using a Bruker Fourier transform n.m.r. spectrometer operating at 25.7MHz for ^{11}B resonance. This is comparable with the instruments used by Henderson and Pasdeloup and their co-workers. The instrumental parameters were optimized as shown in appendix 5.

^{11}B n.m.r. spectra were obtained from 10^{-3} to $10^{-2}M$ solutions of boric acid in 90% v/v sulphuric acid in less than 10 minutes as the short relaxation time of ^{11}B nuclei enabled a fast pulse repetition rate (< 1 sec) to be used. The spectra of more dilute solutions, of similar concentration to those used for the fluorimetric work (10^{-5} to $10^{-4}M$ boric acid), however, would have required overnight runs to obtain satisfactory signal to noise characteristics. This was not possible due to lack of instrument availability. Consequently all the following n.m.r. spectroscopy was carried out at the higher range of boric acid concentrations. Although the concentrations at which spectra could be obtained were above those used for fluorimetric work they were below that at which polymeric boron species have been reported ($10^{-1}M$ boric acid).

Solvent effects on chemical shifts of ^{11}B resonances are negligible except where a chemical reaction occurs so that chemical shifts for boron compounds can be regarded as characteristic constants for identification purposes. It was possible to deduce, from chemical shifts, information about the bonds between boron and adjacent atoms in the molecules investigated. Chemical shifts were related to boron trifluoride diethyletherate, $BF_3O(C_2H_5)_2$, the liquid generally accepted as the external zero reference for boron n.m.r. spectroscopy because of its sharp resonance line. The resonance occurs in the chemical shift region corresponding to compounds containing tetrahedral boron atoms (chemical shift,δ,5ppm to -40ppm; a shift to lower fields is referred to as positive in this work). In practice an aqueous boric acid solution was used as the external reference as the resonance obtained had a shift of 19.4ppm to lower field and was thus clear of the region of the spectrum being studied. This low field chemical shift indicates less shielding of the boron atom than is the case with the tetrahedral zero reference, $BF_3O(C_2H_5)_2$, and is typical of the shift occurring when three oxygens are bound to a trigonal boron atom (88).

The reference solution was contained in a 3mm diameter tube held concentric with a 10mm diameter sample tube by passing through the cap and a vortex spoiler. The annulus between the tubes was used to hold the sample solution being investigated. The reference solution also contained D_2O to provide a lock signal for the spectrometer.

4.1.1 Effect of variation of sulphuric acid concentration on boron resonance

A series of n.m.r. spectra were recorded for solutions of 10^{-2}M boric acid in various concentrations of sulphuric acid. The chemical shifts and line widths are shown in the graphs - Figure 4.1.

Two resonances were observed for acid concentrations greater than 80% v/v (50 mole percentage) sulphuric acid (Figure 4.2). One was a narrow line with a chemical shift of -3.4ppm which was not affected by acid concentration. The intensity of this resonance decreased rapidly with decreasing sulphuric acid concentration. The second resonance was broader and increased in width and intensity with decreasing acid concentration. The chemical shift was dependent on the acidity, initially at -2.4ppm it moved down field with decreasing acid concentration. At acid concentrations less than 80% v/v this was the only observed resonance. The line width reached a maximum value at around 60 to 70% v/v (30 to 40 mole%) sulphuric acid. At acid concentrations below 20% v/v (10 mole%) the chemical shift was the same as that of aqueous boric acid. The resonance at -3.4ppm with line half width of 12Hz is typical of a symmetrical tetrahedral coordinated boron species in having a narrow line showing very little quadrupolar broadening and a chemical shift typical of sp^3 hybridization. This resonance can be assigned to the tetra(hydrogensulphato) borate anion proposed by Gillespie (78). The n.m.r. spectra show that this anion exists not only in concentrated sulphuric acid but also in more dilute sulphuric acid solutions.

FIGURE 4.1 ^{11}B N.M.R. - CHEMICAL SHIFT AND LINE WIDTH
$10^{-2}M$ BORIC ACID IN SULPHURIC ACID

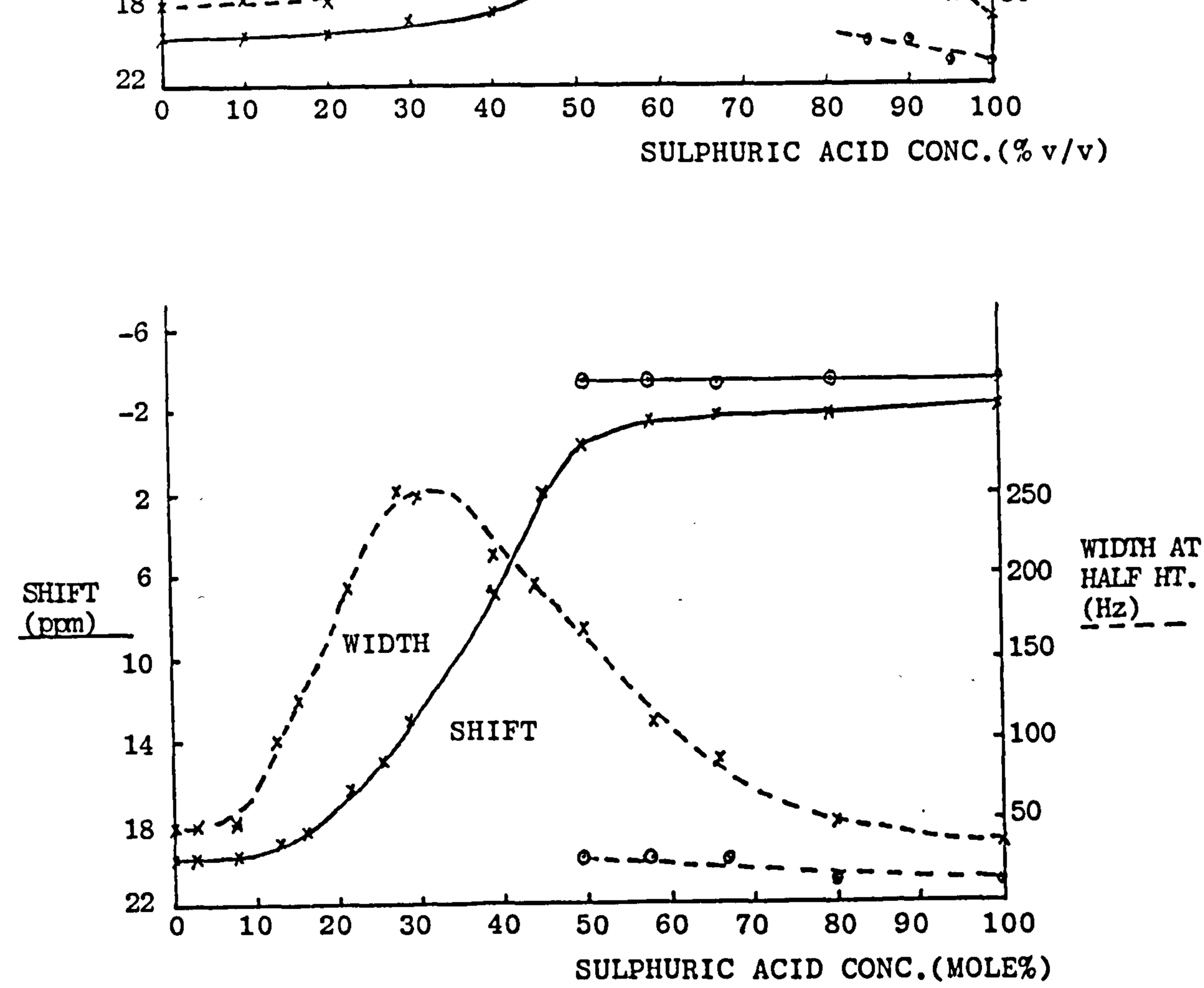
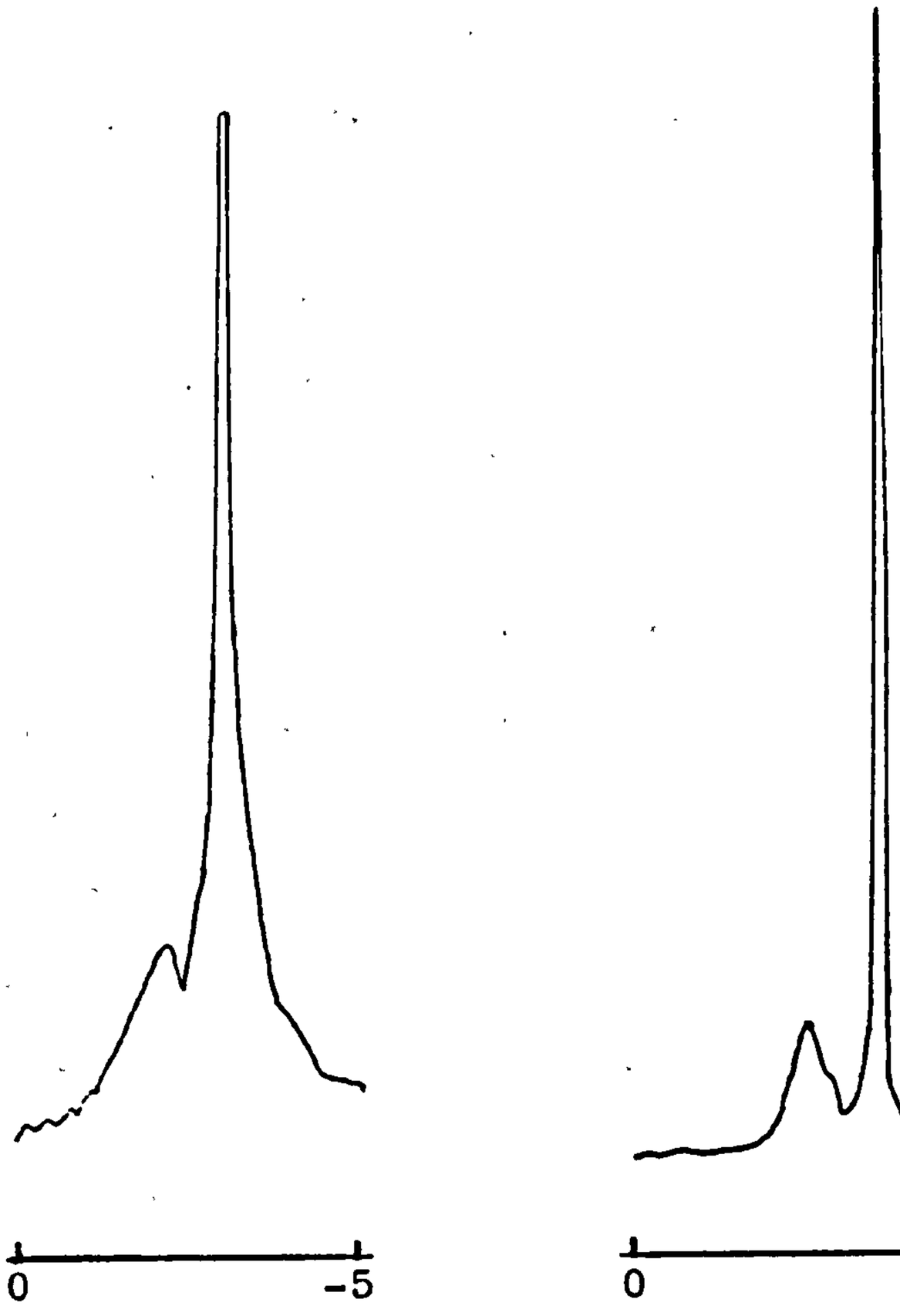
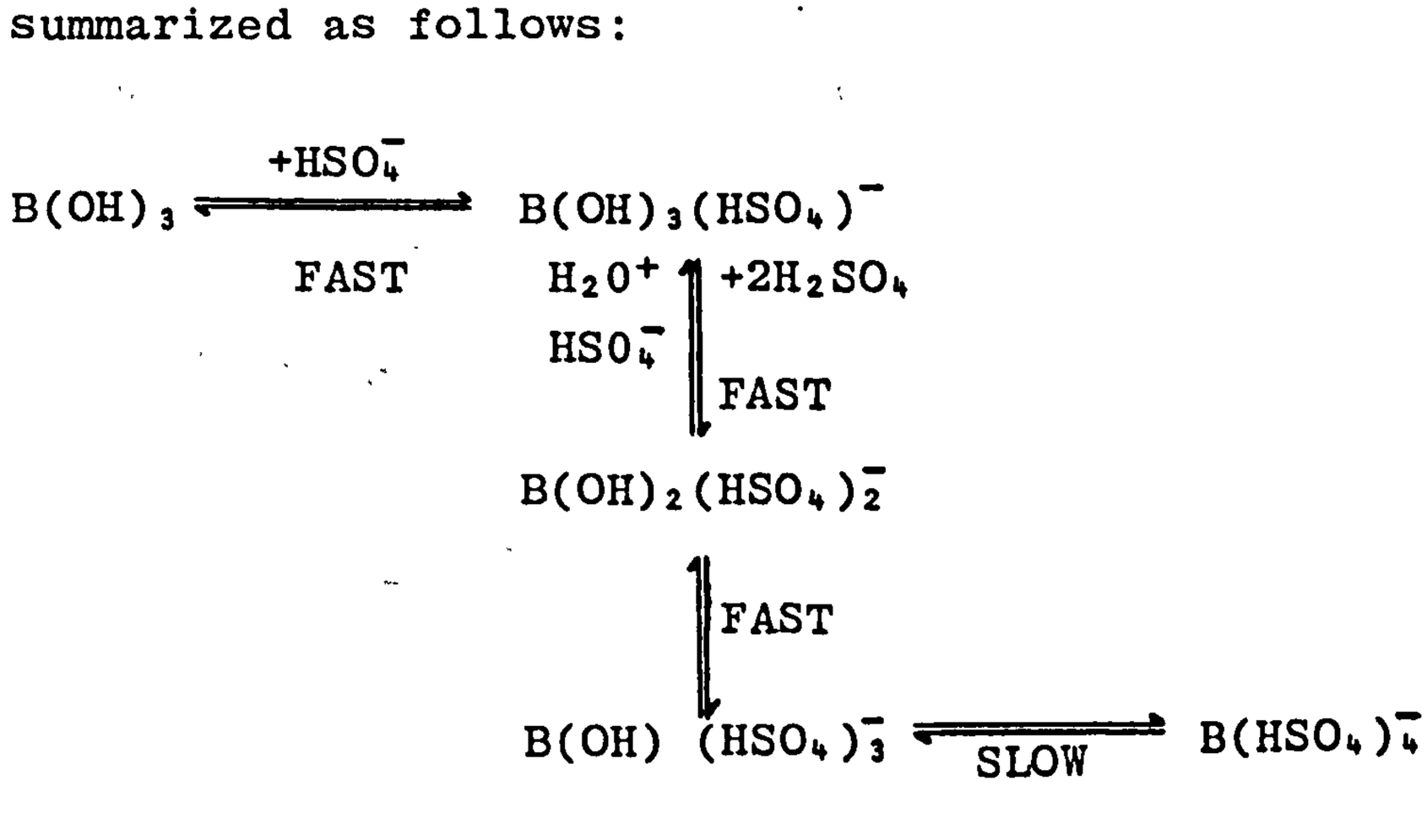


FIGURE 4.2 ^{11}B n.m.r. SPECTRA - BORIC ACID $10^{-2}M$ IN SULPHURIC ACID 95% v/v



The large change in chemical shift of the second resonance indicates a large variation in electronic environment around the boron nucleus as tetrahedral sp^3 hybridization at high sulphuric acid concentrations changes to trigonal sp^2 hybridization in aqueous boric acid solutions. As only one resonance is observed during this process the interconversion must be rapid on the n.m.r. time scale. The line width at half peak height of up to 250Hz at intermediate sulphuric acid concentrations indicates that the rapid interconversion involves more than two species. The most probable species giving rise to this second resonance at high sulphuric acid concentrations is $B(OH)(HSO_4)_3^-$, a tetrahedral but not symmetrical entity and thus subject to quadrupolar broadening. This is consistent with the observed line width at half height of 40Hz. In aqueous solutions boric acid is present as trigonal $B(OH)_3$, while at intermediate sulphuric acid concentrations the line width is consistent with the presence of species such as $B(OH)_2(HSO_4)_2^-$ and $B(OH)_3(HSO_4)^-$ and with rapid exchange of OH and HSO_4 radicals occurring between all the hydroxy-containing species.

The n.m.r. data suggest that the equilibria occurring between boric acid and increasing concentrations of sulphuric acid may be summarized as follows:



4.1.2 Stability constants of boric acid complexes from ^{11}B n.m.r.

^{11}B n.m.r. spectra obtained from solutions containing equimolar amounts of boric acid and thoron in sulphuric acid concentrations of 70 to 100% v/v showed decreases in intensity of the borate anion resonances but no resonance from the boric acid - thoron complex could be distinguished.

In 95% v/v sulphuric acid the decrease in intensity of the sharp line at -3.4ppm was most pronounced. Calibrations constructed from the height, or area, of this peak ratioed to the signal from the aqueous boric acid external standard and plotted against the corresponding boric acid concentration showed a nearly linear relationship (Figure 4.3). These were used to obtain the apparent stability constant of the boric acid - thoron complex based on the decrease in the uncomplexed boric acid concentration in the thoron - containing solutions calculated from the change in the $B(HSO_4)_4^-$ resonance.

The stability constant was obtained, as in the fluorimetric work, from the relationship

$$\beta_1 = \frac{AB}{(A_o-AB)(B_o-AB)}$$

when A is the measured 'free' boric acid concentration obtained from the $B(HSO_4)_4^-$ n.m.r. peak

$$\beta_1 = \frac{AB}{A(B_o-AB)}$$

$$= \frac{(A_o-A)}{A[B_o-(A_o-A)]}$$

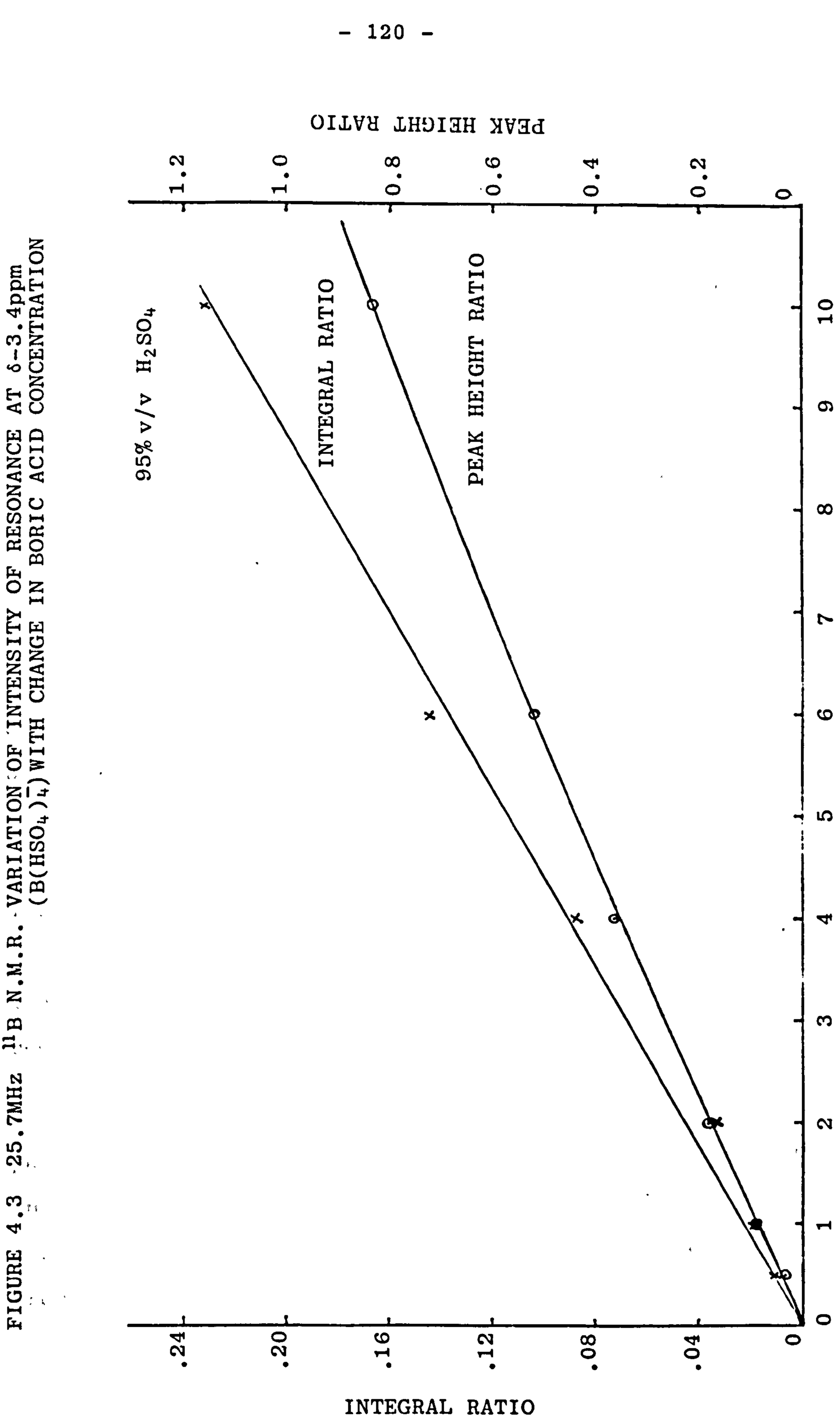


FIGURE 4.3 25.7MHz ^{11}B N.M.R. - VARIATION OF 'INTENSITY OF RESONANCE AT δ-3.4ppm ($B(HSO_4)_4^-$) WITH CHANGE IN BORIC ACID CONCENTRATION

The apparent stability constants obtained from this calculation are given in the table Figure 4.4. The values are lower than, but of the same order, as those found from the fluorimetric measurements. Greater reproducibility was found using peak height measurements than was obtained from peak area measurements. The measured resonance at -3.4ppm and that at -2.4ppm assigned to $B(OH)(HSO_4)_3^-$ are not fully resolved and there was thus some ambiguity in the integrated peak area values which were obtained using this instrument.

4.2 ^{11}B n.m.r. at 128MHz

The 25.7MHz ^{11}B n.m.r. spectra show that information on complex formation can be obtained from n.m.r. measurements, but the resolution obtainable was insufficient for the various boric acid - sulphuric acid species and the boric acid - thoron complex to be seen as separated peaks. However, the opportunity arose to use the Bruker high field (9.4T) n.m.r. spectrometer at Warwick University which uses a superconducting magnet and has a proton resonance frequency of 400MHz. For ^{11}B nuclei the resonance frequency was 128MHz.

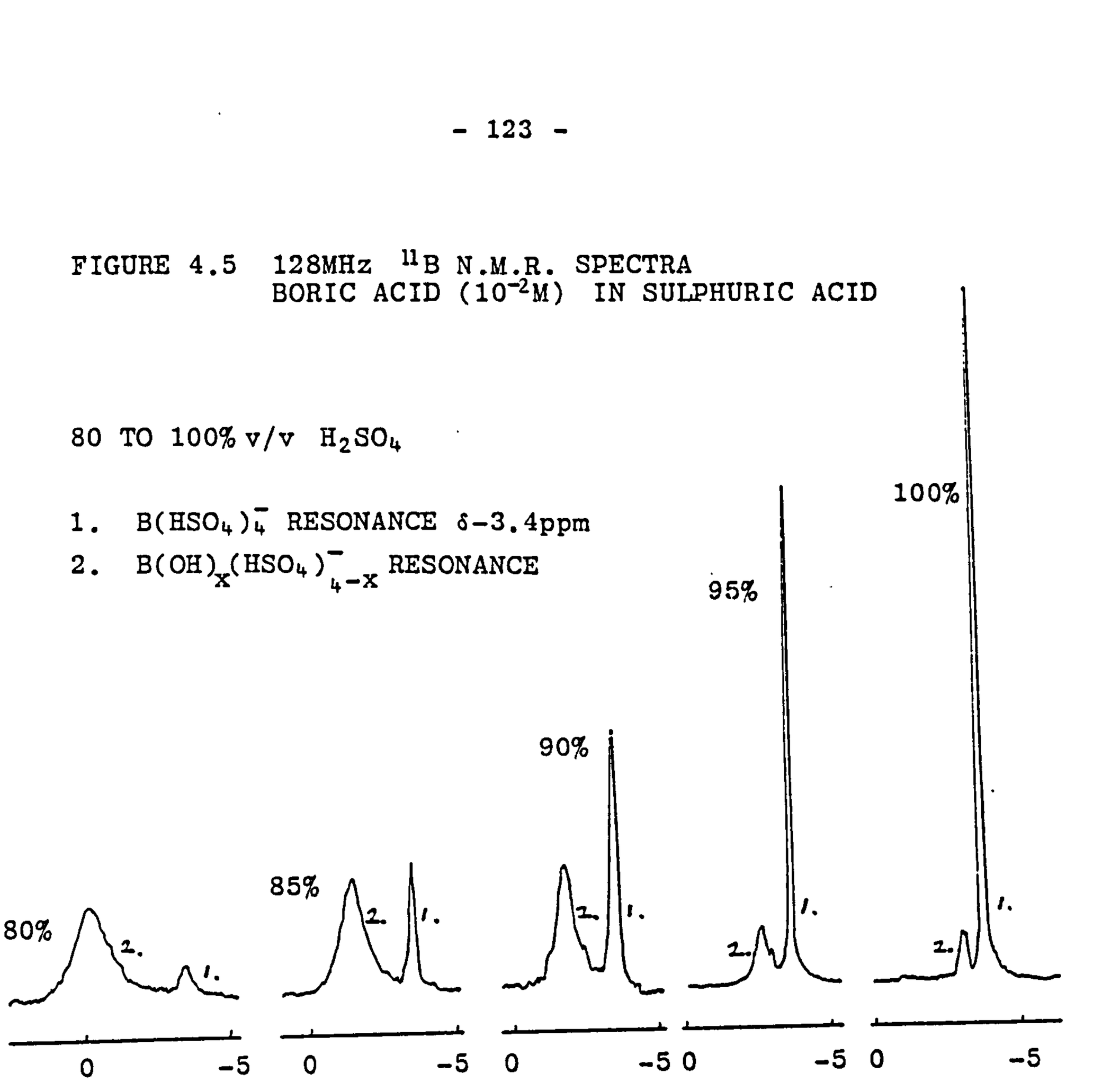
The spectra obtained from this instrument showed distinct peaks for $B(HSO_4)_4^-$ at δ = -3.4ppm, the postulated $B(OH)_x(HSO_4)_{4-x}^-$ species, with varying shift values (Figure 4.5), and for the first time a separate resonance was obtained for the boric acid - thoron complex (Figure 4.6).

FIGURE 4.4 BORIC ACID THORON APPARENT STABILITY CONSTANT
^{11}B n.m.r. at 25.7MHz

BORIC ACID CONC. /10^{-3}M	THORON CONC. /10^{-3}M	PEAK AREA			UNCOMPLEXED BORIC ACID CONC./10^{-3}M	APPARENT STABILITY CONST. /$10^{-3}M^{-1}$
		BORIC ACID IN 95% H_2SO_4	BORIC ACID AQ. REF.	RATIO		
0.5	0	2.12	206	.010		
1		2.5	131	.019		
2		4.5	132	.034		
4		11	126	.087		
6		18	125	.144		
10		32	139	.230		
10	10	10.5	128	.082	3.6	0.49
		9.5	129	.074	3.3	0.62
		8.0	130	.061	2.7	1.0
10	5	20	135	.148	6.4	0.40
4	4	3.8	135	.028	1.3	1.60

		PEAK HEIGHT				
0.5	0	5	198	.028		
1		18	192	.094		
2		32	184	.174		
4		35	94	.372		
6		47.5	92	.516		
10		87	105	.829		
10	10	20	95	.211	2.50	1.20
		20	96	.208	2.48	1.22
		39	183	.213	2.52	1.18
10	5	47	102	.461	5.48	1.71
4	4	10.3	98	.105	1.25	1.76

FIGURE 4.5 128MHz ^{11}B N.M.R. SPECTRA
BORIC ACID ($10^{-2}M$) IN SULPHURIC ACID



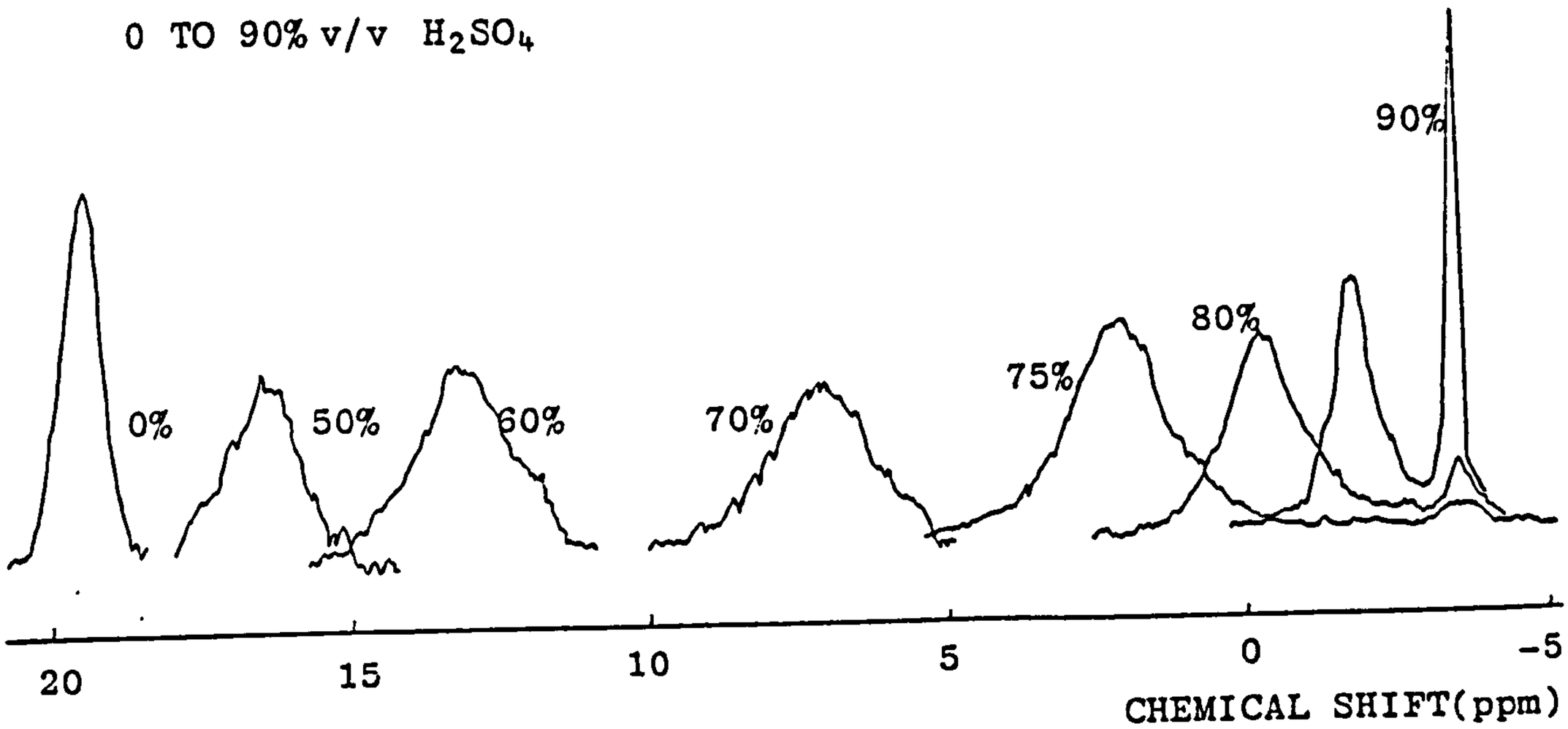
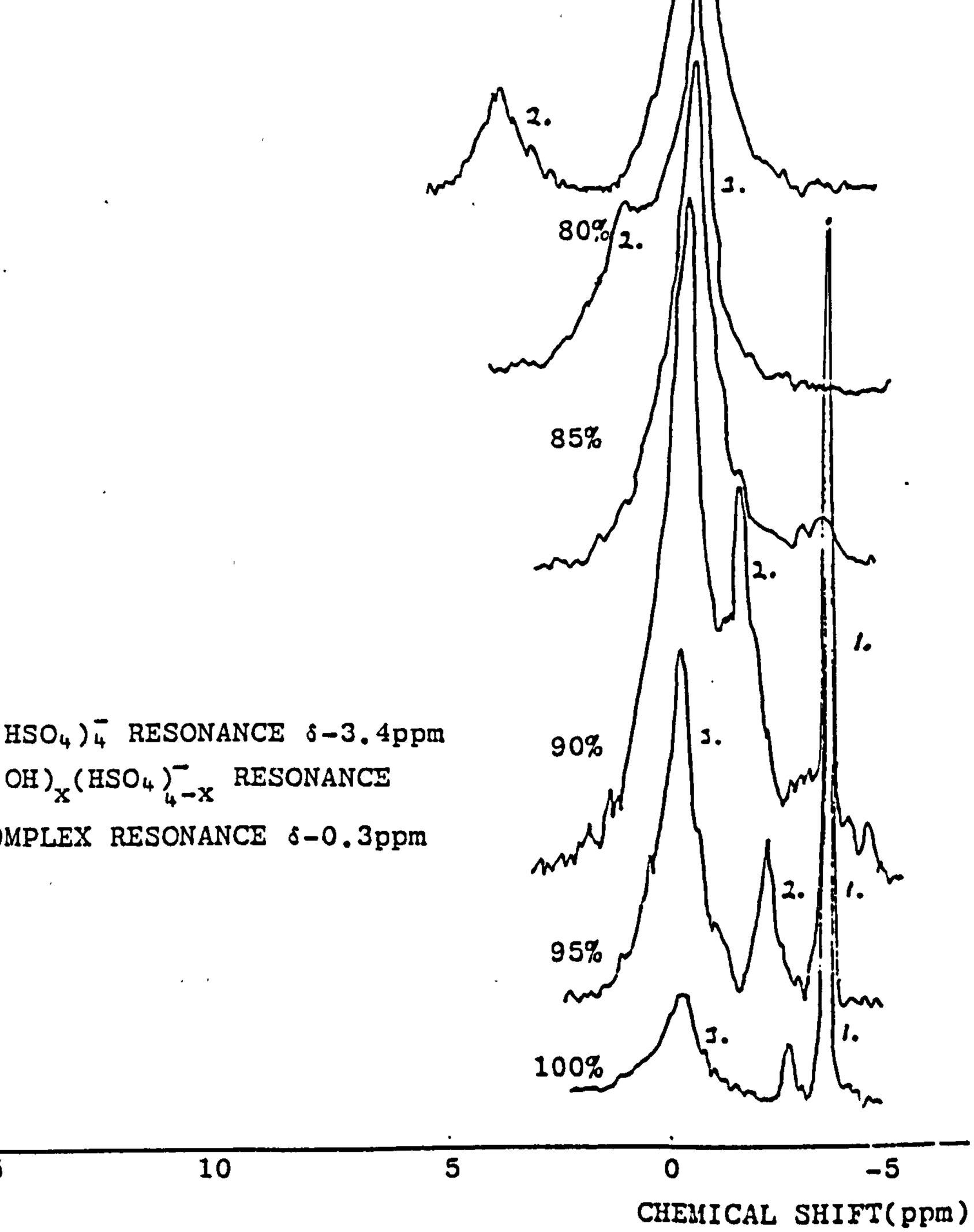


FIGURE 4.6 128MHz ^{11}B N.M.R. SPECTRA
BORIC ACID AND THORON (EQUIMOLAR $10^{-2}M$)
IN SULPHURIC ACID (60 to 100% v/v)



1. $B(HSO_4)_4^-$ RESONANCE δ-3.4ppm
2. $B(OH)_x(HSO_4)_{4-x}^-$ RESONANCE
3. COMPLEX RESONANCE δ-0.3ppm

The chemical shift of the complex resonance, -0.3ppm, is consistent with the boron being present as a tetrahedral species. The position of the peak did not vary with sulphuric acid concentration but the intensity decreased with decreasing sulphuric acid concentration. Below 60% v/v sulphuric acid no resonance was observed from the complex and there was no decrease in intensity of the borate anion resonance.

4.2.1 Stability constants of boric acid complexes from 128MHz ^{11}B n.m.r.

The greater resolution obtained at 128MHz allowed apparent stability constants for the boric acid - thoron complex to be calculated at sulphuric acid concentrations where the boric acid was initially present in significant amounts as the $B(OH)_x(HSO_4)^-_{4-x}$ species, a resonance not resolved at 25.7MHz.

As the resonance assigned to $B(OH)_x(HSO_4)^-_{4-x}$ moved down field with decreasing sulphuric acid concentration the peak passed through the stationary resonance at -0.3ppm produced by the boric acid - thoron complex. At a sulphuric concentration of 85% v/v the peaks were coincident and no data could be obtained from the resonance signal produced by the boric acid - thoron complex (Figure 4.6). At other sulphuric acid concentrations the concentration of the complex could be obtained from the chart integral of the peak compared to the total peak area of all the boron resonances as the total boric acid concentration was known.

The concentration of the complex was also calculated from the decrease in area of both $B(HSO_4)^-_4$ and $B(OH)_x(HSO_4)^-_{4-x}$ resonances

obtained from comparison of solutions containing thoron with solutions containing boric and sulphuric acids only.

The apparent stability constants at various sulphuric acid concentrations obtained from both estimations of complex concentration are given in the table - Figure 4.7. The values are similar for both calculation procedures and are greatest between 70 and 90% v/v sulphuric acid (40 to 65 mole%), at lower concentrations a rapid decrease in stability constant occurred until no complex formation was detected below 60% v/v sulphuric acid (30 mole%).

The values obtained for the stability constant in 95% sulphuric acid are similar to those obtained from earlier measurements of peak areas of 25MHz spectra. The value of the stability constant at 90% sulphuric acid, $10^3 M^{-1}$, is lower than that obtained from fluorescence measurements, $7 \times 10^3 M^{-1}$, but may be considered an acceptable agreement when the difference in concentrations and temperature is considered. For n.m.r. boric acid = thoron = 10^{-2}M temperature 30°C, for fluorescence boric acid = 10^{-4} to 10^{-3}M thoron = 10^{-6}M temperature 25°C. The temperature at the n.m.r. measurement region could not conveniently be reduced from its ambient temperature to match that of the fluorescent work.

4.2.2 ^{11}B n.m.r. Boric acid complexes with 2-hydroxyphenylketones

In order to assess the validity of the n.m.r. work on the stability of the boric acid - thoron complex, the n.m.r. spectra

FIGURE 4.7 STABILITY CONSTANTS BORIC ACID - THORON COMPLEX
128MHz ^{11}B n.m.r.

H_2SO_4 CONC. /%v/v	THORON CONC. /10^{-2}M	PEAK AREA/PEAK AREA OF REF.				COMPLEX CONC. /10^{-3}M		STABILITY CONST /10^3M^{-1}	
		COMPLEX	$B(HSO_4)_4$	$B(OH)_x(HSO_4)_{4-x}^-$	TOTAL	1	2	1	2
100	1	.357	.226	.047	.630	5.67	5.64	.30	.30
"	0	-	.552	.082	.634				
95	1	.324	.090	.062	.477	6.79	6.81	.66	.67
"	0	-	.420	.250	.670				
90	1	.452	.043	.122	.617	7.32	7.33	1.02	1.03
"	0	-	.295	.176	.471				
85	1	-	.023	-	.543	-	7.83	-	1.66*
"	0	-	.094	.385	.480				
80	1	.458	.000	.120	.578	7.92	7.72	1.83	1.49
"	0	-	.049	.519	.568				
75	1	.355	.000	.098	.453	7.84	7.66	1.68	1.40
"	0	-	.008	.475	.483				
70	1	.265	.000	.074	.339	7.82	7.82	1.65	1.65
"	0	-	.000	.367	.367				
65	1	.805	.000	.708	1.513	5.32	5.32	0.24	0.24
"	0	-	.000	1.771	1.771				
60	1	.281	.000	.825	1.106	2.54	2.54	0.05	0.05
"	0	-	.000	1.355	1.355				

BORIC ACID = 10^{-2}M REF. = AQUEOUS BORIC ACID EXTERNAL STD.

SOLUTIONS EQUILIBRATED 24HRS AT 25°C

* COMPLEX PEAK NOT RESOLVED AT 85% H_2SO_4

1 CALCULATED FROM AREA OF COMPLEX RESONANCE

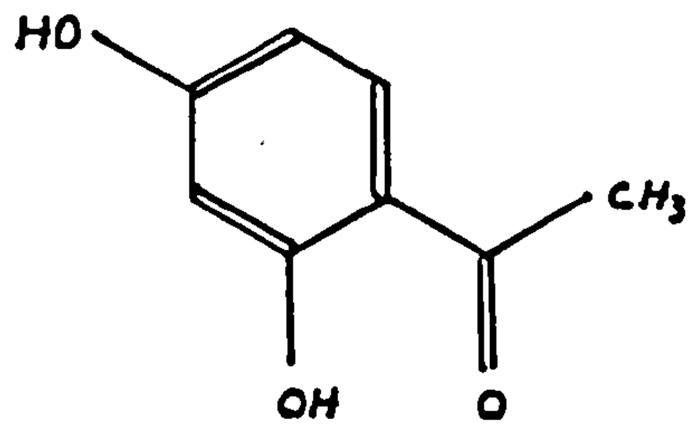
2 CALCULATED FROM AREA OF BORIC ACID RESONANCES

of several 2-hydroxyphenylketones which had previously been shown to form complexes with boric acid in sulphuric acid were obtained, again using the 128MHz instrument.*(41)*

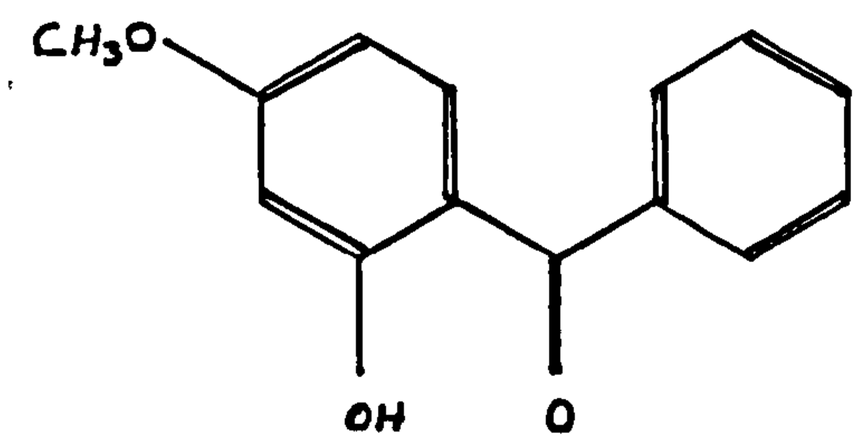
The compounds investigated were 2,4-dihydroxyacetophenone, 2-hydroxy-4-methoxybenzophenone,(HMB), 2-hydroxy-4-methoxy-4'-methylbenzophenone,(HMMB) and 2-hydroxy-4-methoxy-4'-chlorobenzophenone,(HCMB) (Figure 4.8). The solutions were prepared and equilibrated in the same way as for the formation of the thoron - boric acid complex.

All the compounds were found to give a single n.m.r. peak which could be attributed to a complex with boric acid. (Figure 4.9) The chemical shift values of the complexes are given in the table - Figure 4.10. They are all similar to that of the thoron - boric acid complex indicating a similar electronic environment for the boron atom in all the complexes. As with the thoron complex the chemical shift of the complexes were only slightly affected by the sulphuric acid concentration of the media. The n.m.r. spectra of the boric acid complexes with the 2-hydroxyphenylketones in strong sulphuric acid show that they are long lived species compared with the n.m.r. process and do not appear to be in rapid equilibrium with the borate anion species. The spectra also serve to confirm the assignment of the complex resonance in the thoron - boric acid spectra.

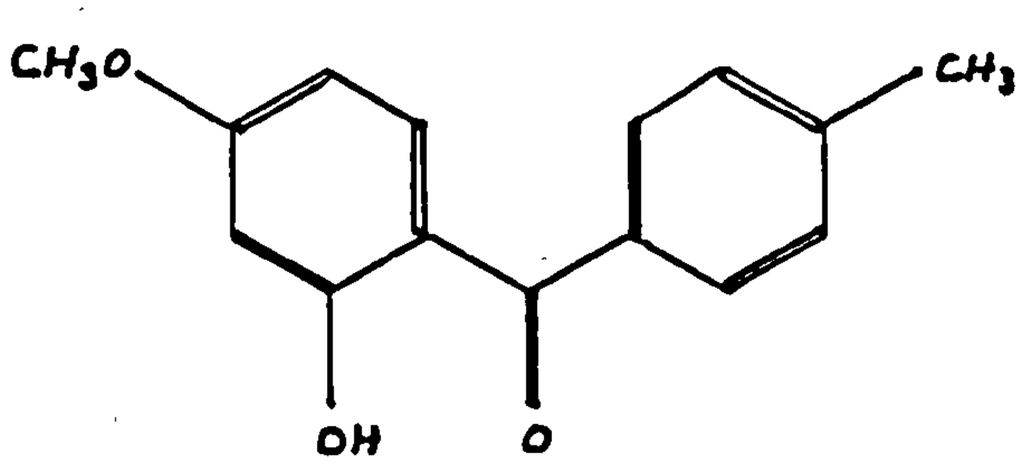
The greater stability of the complexes, when compared with the thoron - boric acid complex, resulted in a comparatively small residual resonance from the uncomplexed borate anions when equimolar solutions of boric acid and complexing reagent



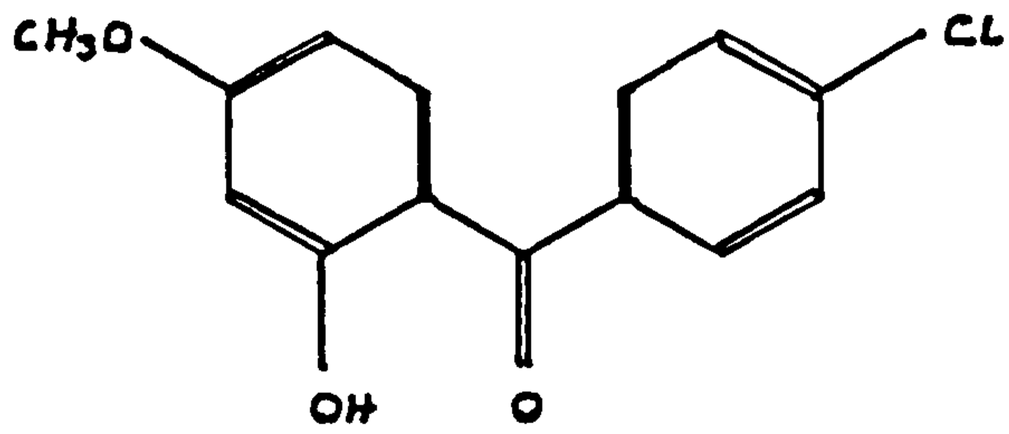
RESACETOPHENONE



HMB 2-HYDROXY-4-METHOXYBENZOPHENONE



HMMB 2-HYDROXY-4-METHOXY-4'-METHYLBENZOPHENONE



HCMB 2-HYDROXY-4-METHOXY-4'-CHLOROBENZOPHENONE

FIGURE 4.8

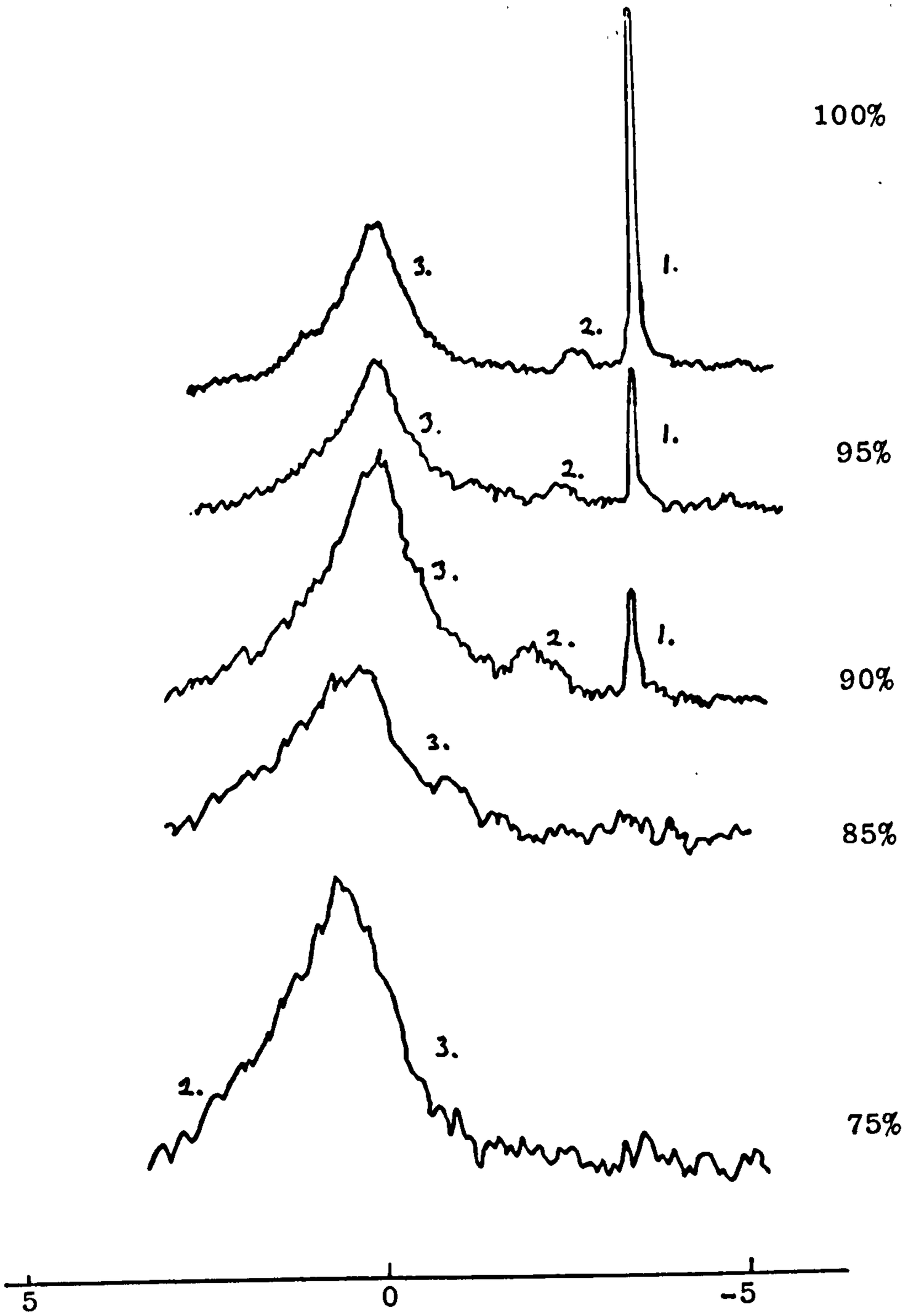
FIGURE 4.9

128MHz ^{11}B N.M.R. SPECTRA

$10^{-2}M$ BORIC ACID

$10^{-2}M$ HCMB

SULPHURIC ACID 75 - 100% v/v



1. $B(HSO_4)_4^-$ RESONANCE δ-3.4ppm
2. $B(OH)_x(HSO_4)_{4-x}^-$ RESONANCE
3. COMPLEX RESONANCE δ 0.0ppm

FIGURE 4.10 128MHz ^{11}B N.M.R. BORIC ACID COMPLEXES WITH 2-HYDROXYPHENYLKETONES

REAGENT	CHEMICAL SHIFT OF BORIC ACID COMPLEX/ppm	APPARENT STABILITY CONSTANT /$10^3 M^{-1}$	
		95% H_2SO_4	90% H_2SO_4
Dihydroxyacetophenone	-0.27	-	4.8
HMB	-0.03	13	1.7
HMMB	-0.06	13	6.8
HCMB	-0.01	11	7.4
(Thoron	-0.30	0.7	1.0)

were studied. Combined with the greater line widths (about 130Hz at half height) this resulted in the complex resonance overlapping that of the uncomplexed borate between 75% and 85% v/v sulphuric acid concentrations, consequently no data on the stability of the complexes could be extracted.

At higher sulphuric acid concentrations the resonances were resolved and the values of the apparent stability constants obtained are given in Figure 4.10. The values show that the complexes formed by the 2-hydroxyphenylketones are more stable than that formed by thoron.

The values of the apparent stability constants of thoron and HCMB boric acid complexes were both lower when determined by n.m.r. measurements than when based on fluorimetric data. The discrepancy is in both instances less than an order of magnitude and while n.m.r. measurements may be subject to uncertainty in the measurement of peak areas when the peaks are not well resolved, the results may be considered sufficiently precise for the relative stability of various complexes of boric acid in sulphuric acid media to be established and to support the validity of the fluorescence derived stability constants.

4.2.3 N.m.r. investigation of effect of iron on the thoron - boric acid complex

The addition of iron(II) to sulphuric acid solutions containing thoron and boric acid had previously been found to slightly alter the intensity of the emitted fluorescence, (see section 2.4.1). In order to further investigate the effect of

iron on the formation of the thoron - boric acid complex the n.m.r. spectra of the borate anion species and of the thoron complex were obtained from solutions to which equimolar and excess iron(II) had been added as iron(II) sulphate. These spectra showed only the resonances previously detailed for iron - free solutions (Figures 4.11, 4.12). The resonances were broadened and shifted increasingly to low field with increasing iron(II) content. The resonances attributed to the complex and the $B(HSO_4)_4^-$ anion were shifted the same amount (see table - Figure 4.13) by the magnetic shielding effect of the added iron but the resonance of the $B(OH)_x(HSO_4)_{4-x}^-$ species was affected to a greater extent. This results in the complex resonance being unresolved in 90% v/v sulphuric acid in the presence of 5×10^{-2}M Fe(II) while in 80% sulphuric acid the previously unresolved complex resonance is completely separated enabling an estimate of the stability constant to be made (Figure 4.13).

There is no evidence for the existence of an iron(II) - boric acid complex from the n.m.r. spectra and the values of the stability constants of the thoron - boron acid complex are similar in both iron - free and iron - containing solutions indicating that no stable iron(II) - thoron complex is formed. The effect of iron in the fluorescence determination of boron with thoron must therefore be due to internal filter effects rather than to complex formation.

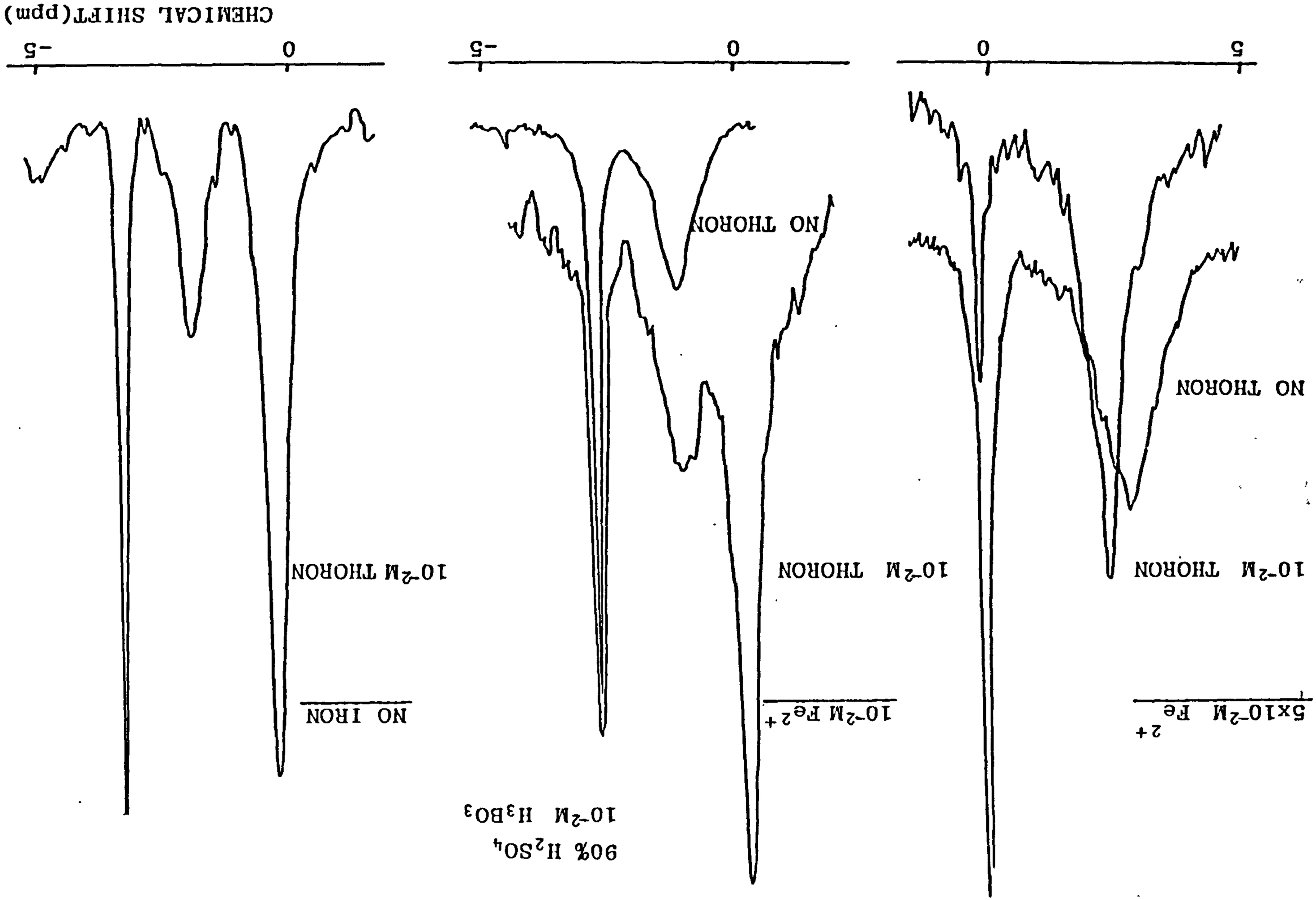


FIGURE 4.11 128MHz ^{11}B N.M.R. SPECTRA BORIC ACID - THORON COMPLEX IN PRESENCE OF Fe^{2+}

FIGURE 4.12 128MHz ^{11}B N.M.R. SPECTRA BORIC ACID - THORON COMPLEX IN PRESENCE OF Fe^{2+}

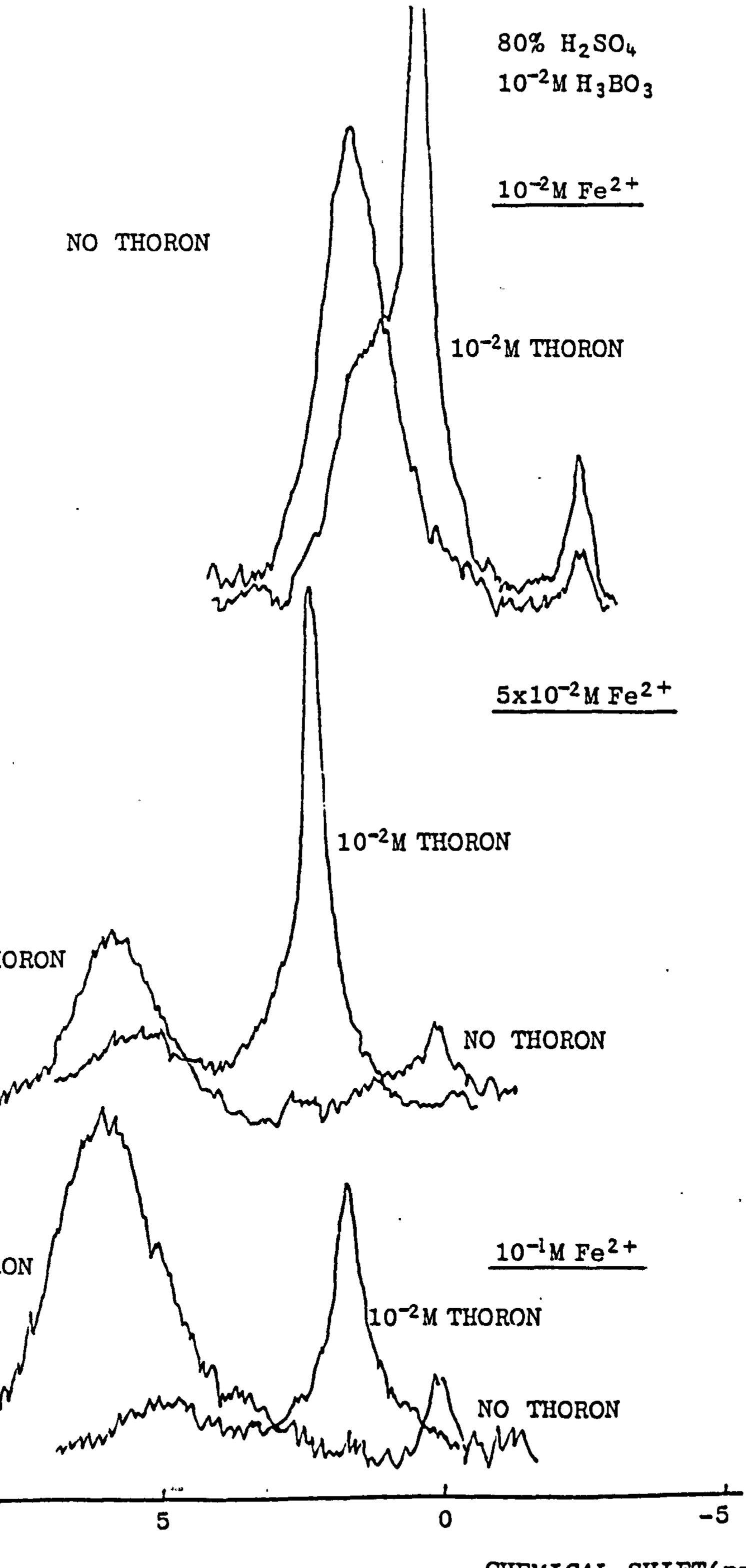


FIGURE 4.13 BORIC ACID - THORON COMPLEX. EFFECT OF IRON(II) ON N.M.R. CHEMICAL SHIFT AND STABILITY CONSTANT

SULPHURIC ACID CONC /% v/v	IRON(II) CONC. /10^{-2}M	THORON CONC. /10^{-2}M	CHEMICAL SHIFT/ppm			STABILITY CONST. /$10^{3}M^{-1}$
			COMPLEX	$B(OH)_x(HSO_4)^-_{4-x}$	$B(HSO_4)^-_4$	
90	0	1	-0.4	-2.0	-3.4	0.4
90	1	1	+0.1	-1.1	-2.8	0.5
	1	0	-	-1.2	-2.8	-
90	5	1	+2.2	+2.7	-0.2	COMPLEX UNRESOLVED
	5	0	-	+2.7	-0.3	-
80	0	1	-0.4	+0.7	-3.2	0.9
80	1	1	+0.1	+1.1	-2.8	1.2
	1	0	-	+1.2	-2.7	-
80	5	1	+2.0	+5.2	-	0.7
	5	0	-	+5.7	0.0	-
80	10	1	+2.3	+4.9	0.0	1.2
	10	0	-	+4.7	-0.3	-

4.2.4 Investigation of n.m.r. spectra of some simple dihydroxy compounds

The ^{11}B n.m.r. spectra of solutions of some dihydroxy and/or azophenyl compounds were obtained from solutions equimolar with $10^{-2}M$ boric acid in 90% v/v sulphuric acid. The compounds investigated were considered simple precursors of the fluorimetric reagents investigated earlier in this work. It was thought that the study of the reaction of these simpler molecules with boric acid might have led to a better understanding of the mode of formation of the analytically useful complexes.

However, no evidence of complex formation was found using 2,2'-dihydroxyazobenzene, 4-hydroxyazobenzene or 1,2-dihydroxybenzene, although this last compound is known to form complexes with boric acid in dilute acidic media (89) and with borate anions in alkaline media (86).

The n.m.r. spectra of solutions containing chromotropic acid (1,8-dihydroxynaphthalene-3,6-disulphonic acid) were obtained over a range of sulphuric acid concentrations (50-90% v/v). No resonance other than those assigned to the borate anion species were observed. These resonances showed a decrease in intensity in the presence of chromotropic acid indicating that complex formation was taking place but that no stable compound containing either trigonal or tetrahedral boron species was formed. The apparent stability constants calculated from the decrease in intensity of the borate anion resonance were $4.3 \times 10^{3} M^{-1}$ in 90% v/v sulphuric acid, $4.0 \times 10^{3} M^{-1}$ in 80%, $3.3 \times 10^{3} M^{-1}$ in 70% and $0.2 \times 10^{3} M^{-1}$ in 50% sulphuric acid.

4.2.5 N.m.r. investigation of boric acid complexes with chromotropic acid derivatives

It was shown in section 2.2.3 that boric acid formed fluorescent complexes with certain phenylazo derivatives of chromotropic acid. ^{11}B n.m.r. spectra at 128MHz of solutions containing arsenazo I and arsenazo III, which had been prepared similarly to the thoron - boric acid solutions used for n.m.r. spectroscopy, confirmed the formation of the complexes with boric acid.

Other phenylazo derivatives were also investigated (Figure 4.14).

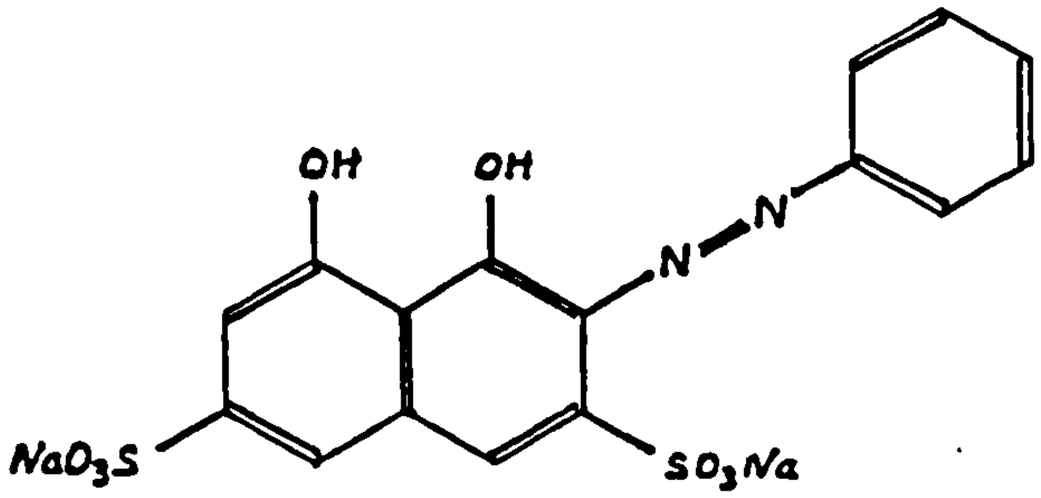
The monophenylazo derivatives chromotrope 2R, SPADNS, both of which have been reported as giving colours with boric acid (90) and arsenazo I each gave a single n.m.r. peak which could be assigned to a complex with boric acid.

The diphenylazo derivatives sulphonazo III and carboxyarsenazo III each gave two resonances associated with a boron complex while arsenazo III gave a n.m.r. spectrum with only one resonance in addition to those of the borate anions. (Figure 4.15).

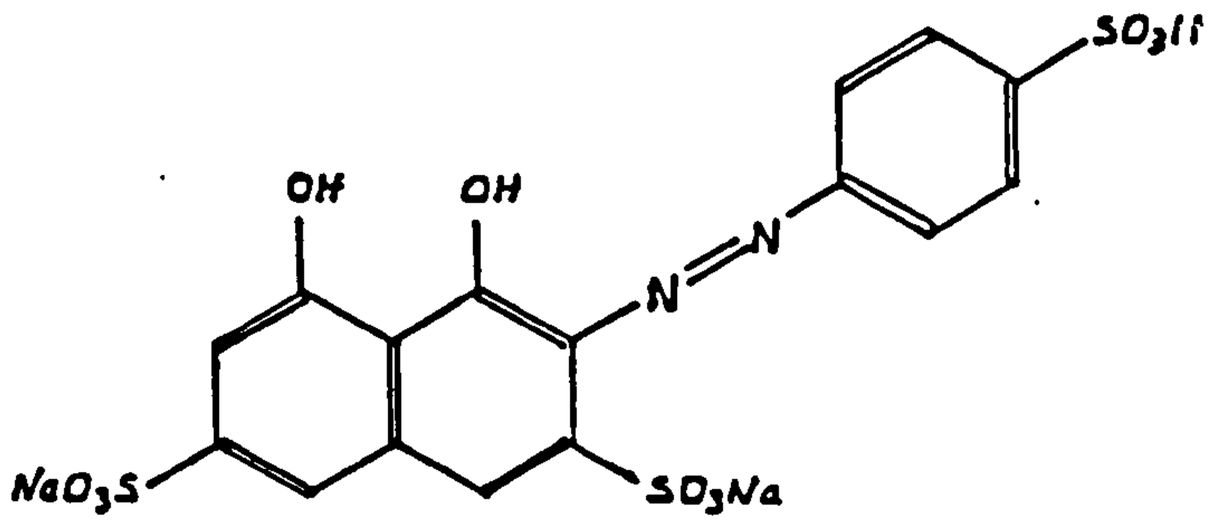
Azomethine H, a condensation product of H-acid (8-amino-1-naphthol-3,6-disulphonic acid) and salicyaldehyde (2-hydroxybenz-aldehyde) gave no indication of a complex in 90% v/v sulphuric acid but showed a resonance from a boric acid complex in 70% v/v sulphuric acid.

The chemical shift values and stability constants are given in Figure 4.16. They were again similar to those obtained with the thoron - boric acid complex.

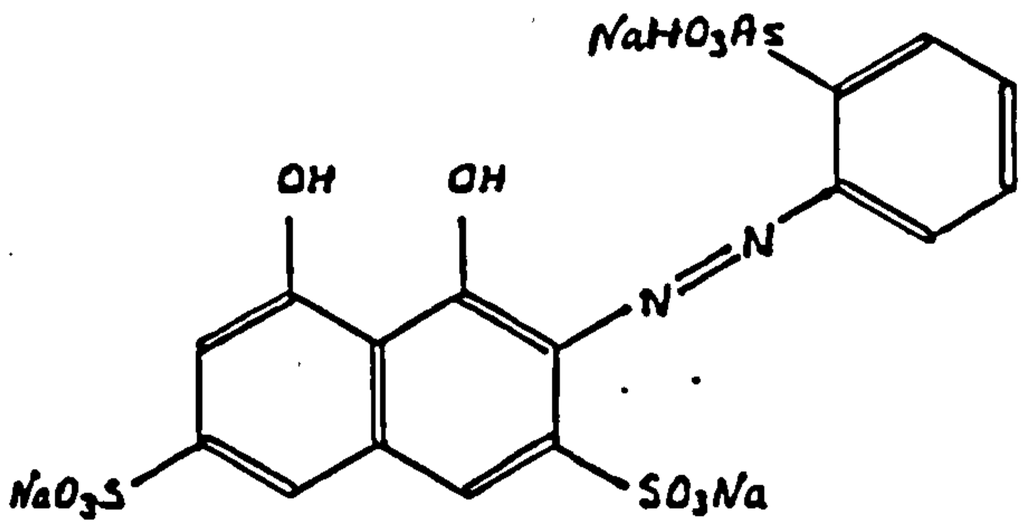
CHROMOTROPE 2R



SPADNS



ARSENAZO I



AZOMETHINE H

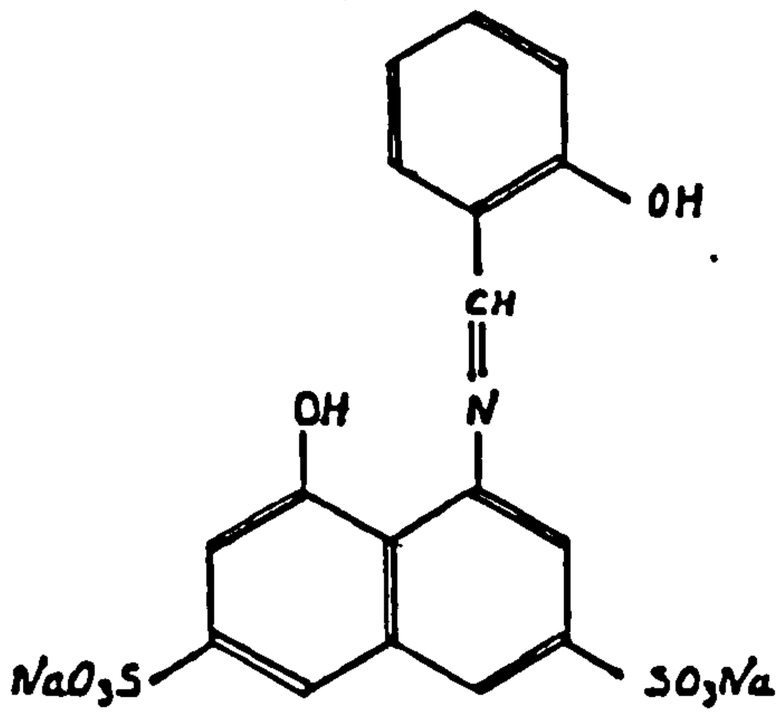
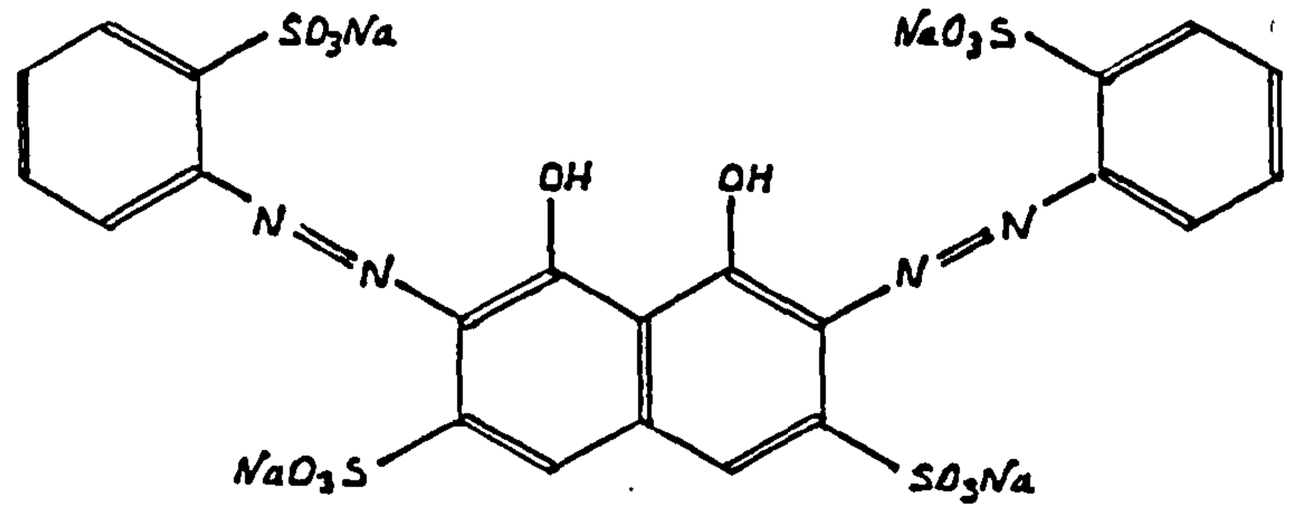
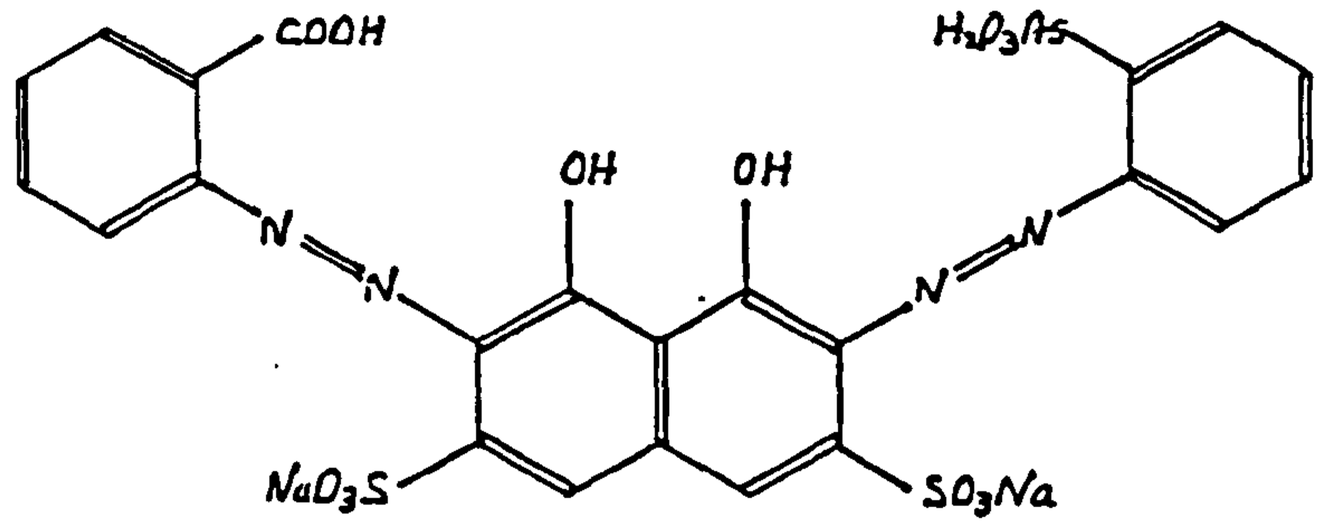


FIGURE 4.14 FORMULAE OF CHROMOTROPIC ACID DERIVATIVES STUDIED USING ^{11}B N.M.R. 128MHz

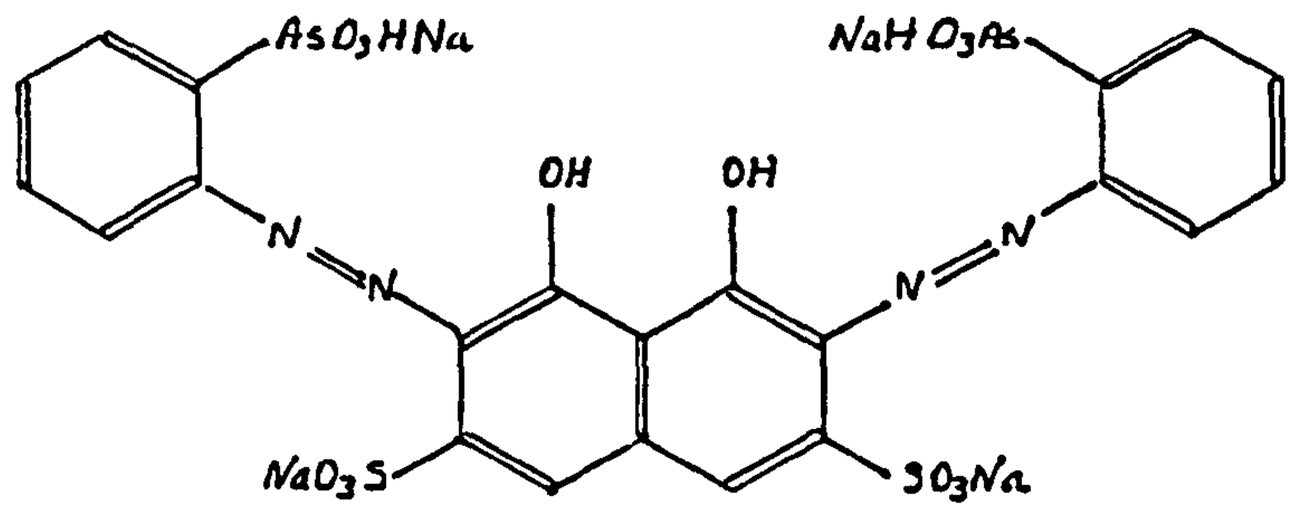
SULPHONAZO III



CARBOXYARSENAZO III



ARSENAZO III



FAST SULPHON BLACK F

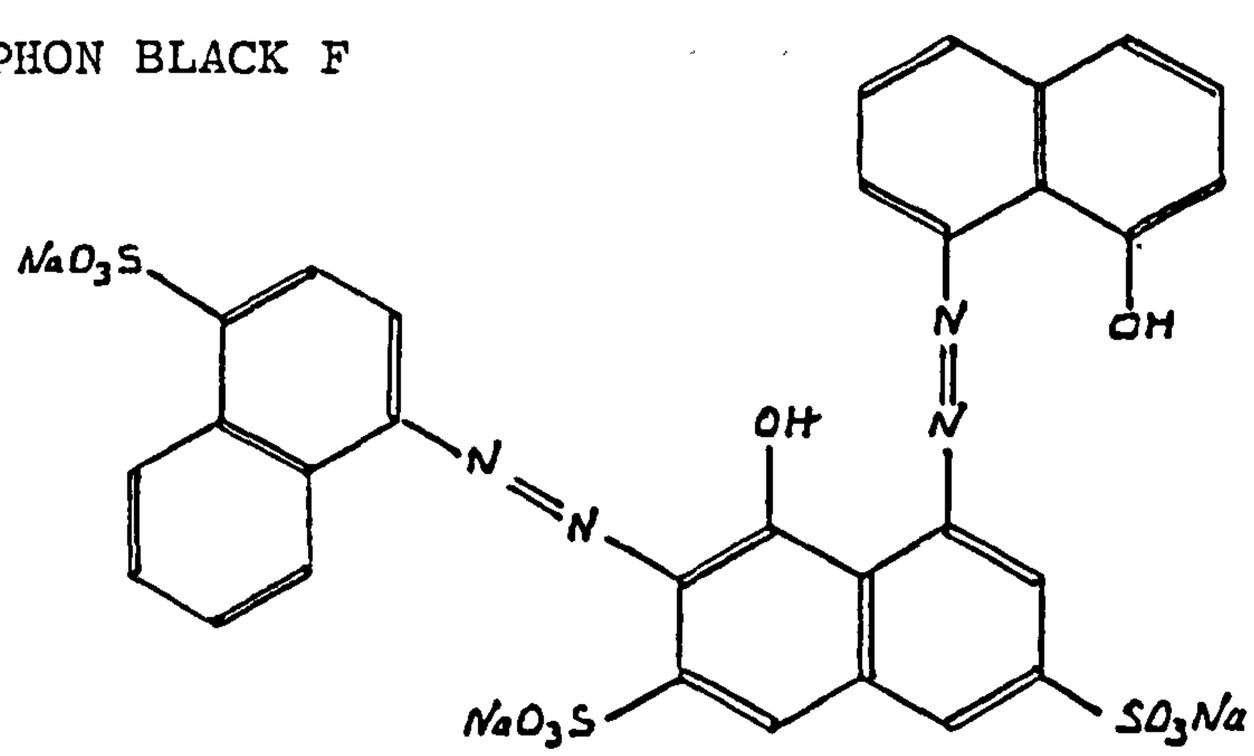


FIGURE 4.14 (CONTINUED)

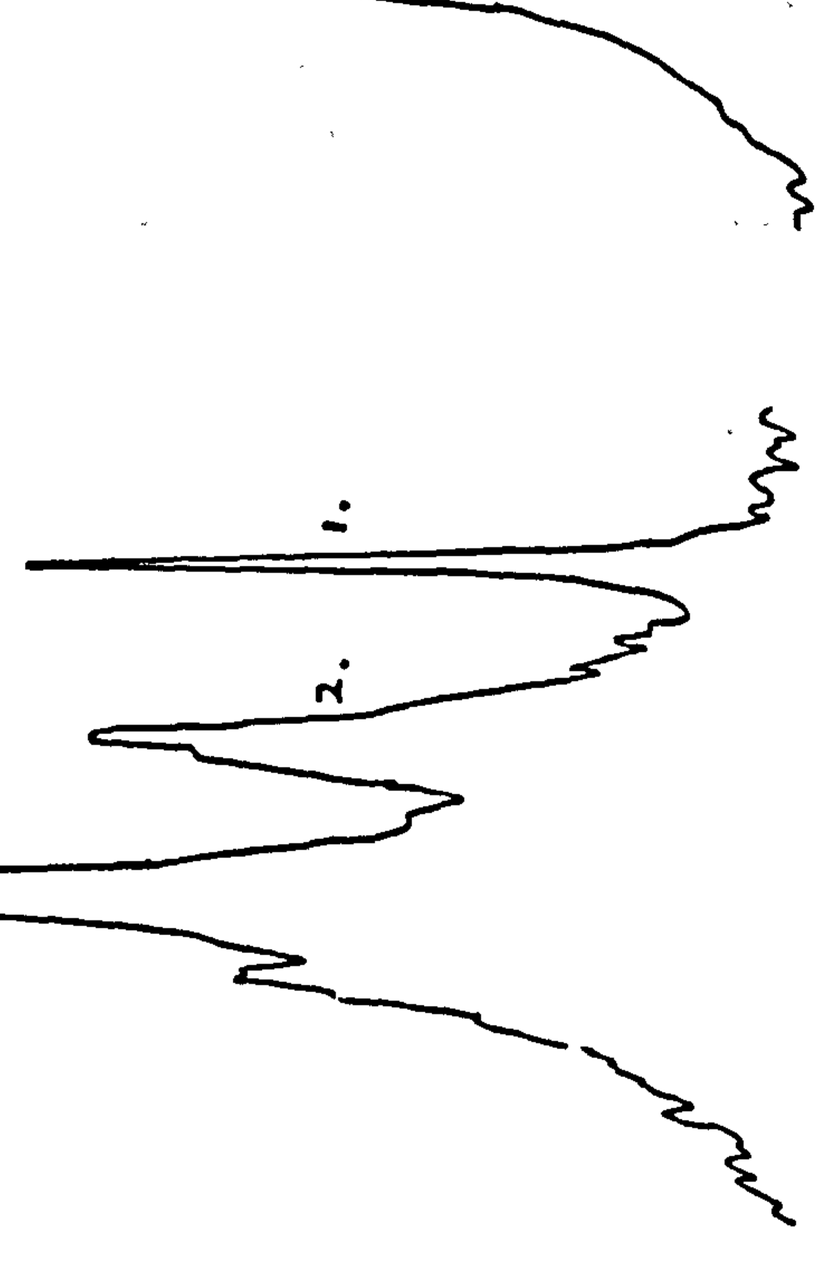
FIGURE 4.15 128MHz ^{11}B N.M.R. SPECTRA OF CHROMOTROPIC ACID BORIC ACID COMPLEXES WITH DIPHENYLAZO DERIVATIVES

SULPHONAZO III

BORIC ACID CONC. 10^{-2}M
REAGENT CONC. 10^{-2}M
SULPHURIC ACID 90% v/v

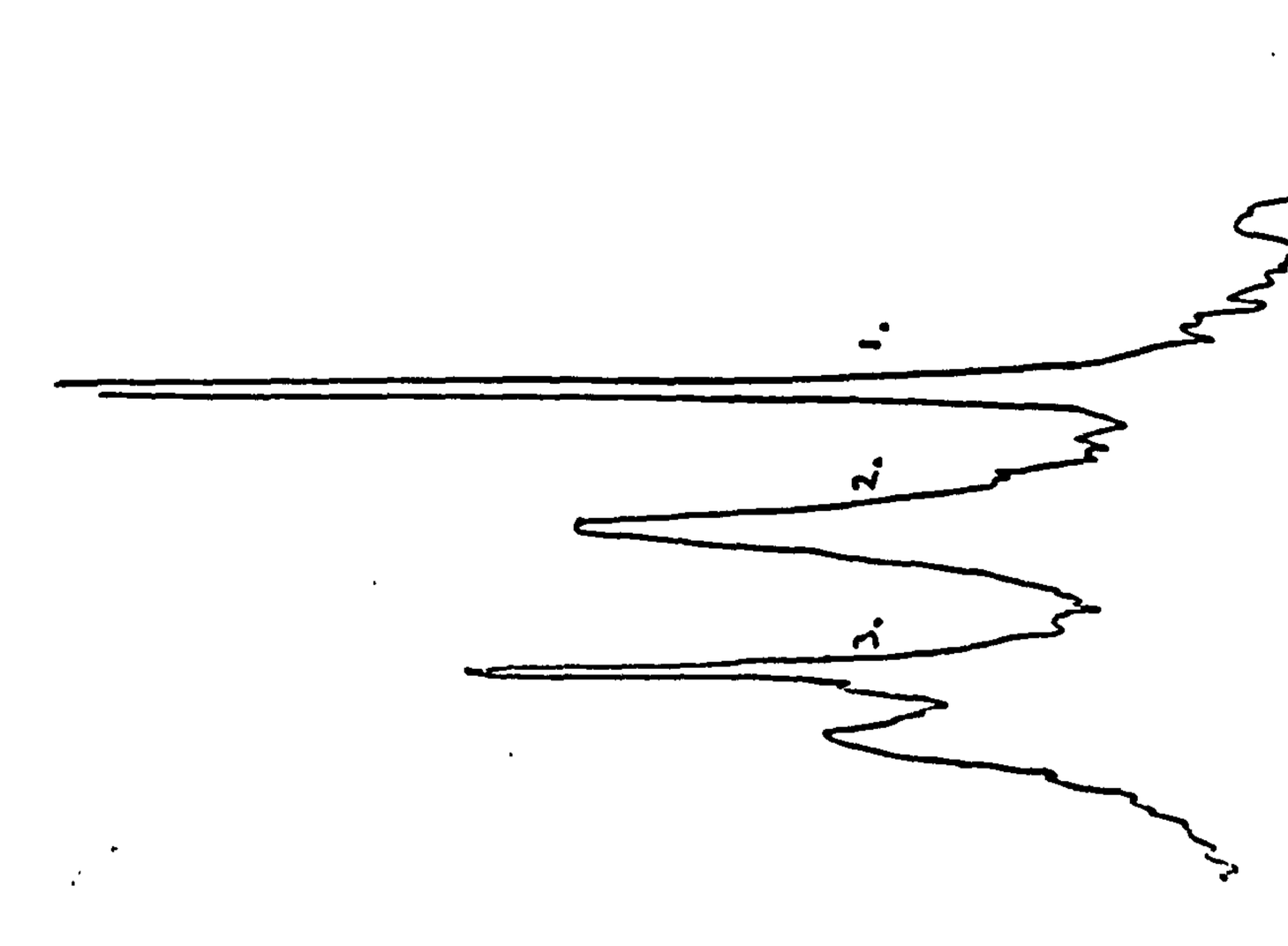
1. $B(HSO_4)_4^-$ RESONANCE δ-3.4ppm
2. $B(OH)_x(HSO_4)_{4-x}^-$ RESONANCE
3. COMPLEX RESONANCE(S)

CARBOXYARSENAZO III



ARSENAZO III

SULPHONAZO III



CHEMICAL SHIFT(ppm)

FIGURE 4.16 128MHz ^{11}B N.M.R. BORIC ACID COMPLEXES WITH CHROMOTROPIC ACID DERIVATIVES. CHEMICAL SHIFTS AND STABILITY CONSTANTS

BORIC ACID 10^{-2}M.
REAGENT 10^{-2}M
SULPHURIC ACID 90% v/v

REAGENT	CHEMICAL SHIFT OF BORON COMPLEX/ppm	APPARENT STABILITY CONST/$10^3 M^{-1}$
CHROMOTROPE 2R	0.0	0.19
SPADNS	-0.1	0.24
ARSENAZO I	-0.2	0.17
SULPHONAZO III	+0.2 -0.6	0.17
CARBOXYARSENAZO III	+0.2 -0.6	0.46
ARSENAZO III	-0.7	0.62
FAST SULPHON BLACK F	NO COMPLEX	-
AZOMETHINE H (in 70%H_2SO_4)	+1.4	0.05

4.3 Discussion

The ^{11}B n.m.r. spectra of boric acid in sulphuric acid medium have confirmed the presence of the tetra (hydrogensulphato) borate anion, $B(HSO_4)_4^-$ in concentrated sulphuric acid which had previously been proposed by Gillespie et al (78,79) from the results of conductiometric measurements

$$B(OH)_3 + 6H_2SO_4 \rightleftarrows B(HSO_4)_4^- + 3H_3O^+ + 2HSO_4^-$$

The resonance of this borate anion was also present in the n.m.r. spectra of boric acid in aqueous sulphuric acid. Its intensity decreased with increasing dilution and the resonance was not detectable below 75% v/v sulphuric acid (80% w/w, 40 mole% approximately) (Figure 4.5). This is consistent with the ionization scheme of Gillespie since, at these dilutions, some undissociated sulphuric acid is known to be present (Figure 4.17) although the equilibrium

$$H_2SO_4 + H_2O \rightleftarrows HSO_4^- + H_3O^+$$

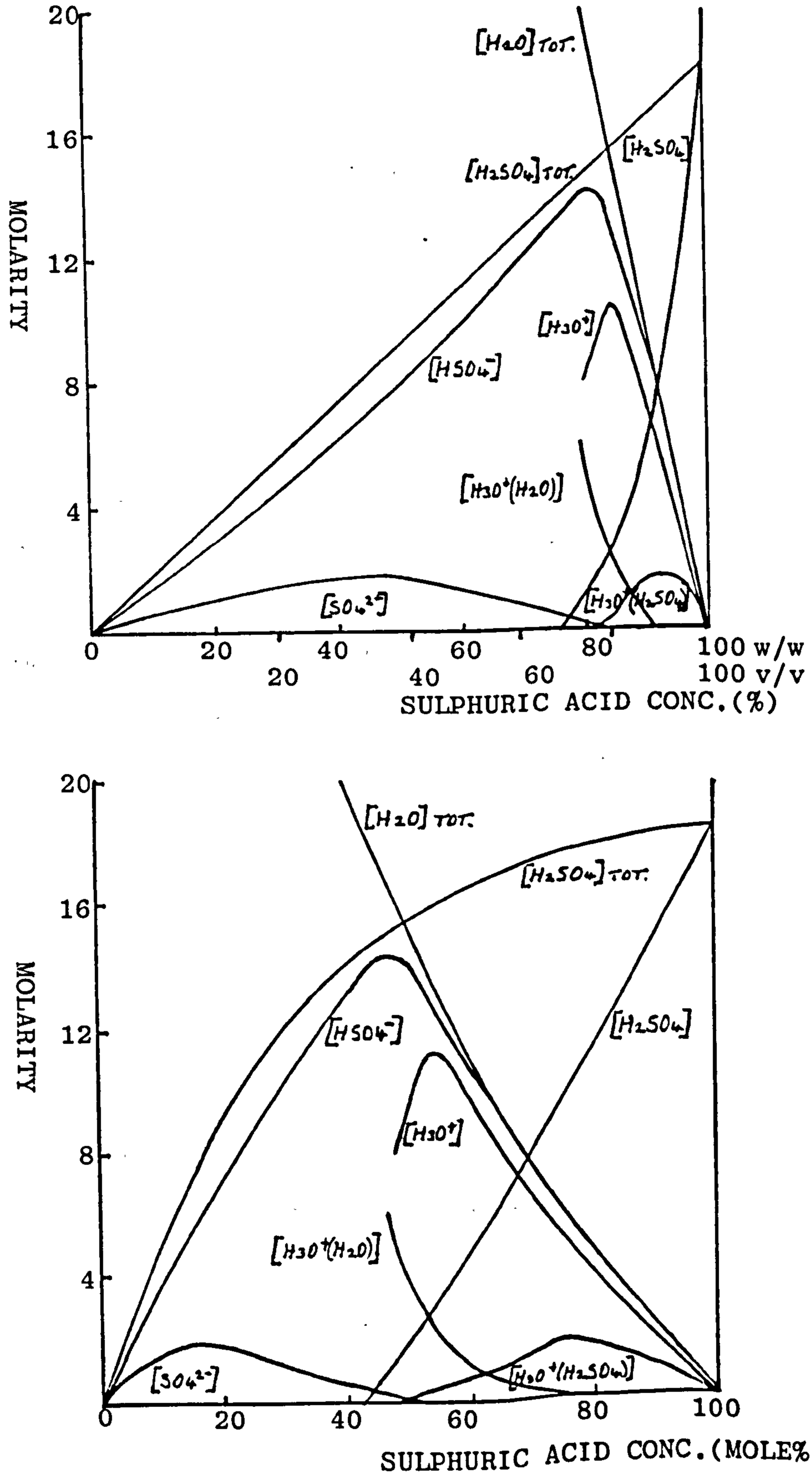
proceeds to completion (91). Solvation of the hydronium ion by water and by sulphuric acid, as below

$$2H_3O^+ + HSO_4^- \rightleftarrows H_3O^+(H_2O) + H_2SO_4$$

$$H_3O^+ + H_2SO_4 \rightleftarrows H_3O^+(H_2SO_4)$$

has been established by Young (93) from Raman measurements.

FIGURE 4.17 SPECIES CONCENTRATIONS - AQUEOUS SULPHURIC ACID AFTER KAANDORP(92) AND YOUNG(93)



The other boron resonance present in the n.m.r. spectra was positioned to low field of the $B(HSO_4)_4^-$ resonance and increased in intensity as the sulphuric acid concentration was reduced and the intensity of the latter resonance decreased. This resonance was assigned to the tetrahedral borate ion $B(OH)_x(HSO_4)_{4-x}^-$. In almost concentrated sulphuric acid this anion may be taken as being predominantly $B(OH)(HSO_4)_3^-$. The formation of this species is favoured by a decrease in sulphuric acid concentration.

$$B(HSO_4)_4^- + H_3O^+ + HSO_4^- \rightleftarrows B(OH)(HSO_4)_3^- + 2H_2SO_4$$

and it is the anion postulated by Marcantonas (64) to account for the increase in rate of complex formation with a lowering of sulphuric acid concentration. The 128MHz ^{11}B n.m.r. spectra of thoron - containing solutions showed a distinct resonance arising from a thoron - boric acid complex in which the boron atom was present in a tetrahedral state. The chemical shift of the complex peak did not change on decreasing the sulphuric acid concentration and the resonance was apparent at below 60% v/v sulphuric acid although at reduced intensity (Figure 4.6) This is a dilution of sulphuric acid greater than that at which the $B(HSO_4)_4^-$ anion has been found to be present. Similar results were obtained from the spectra of boric acid and substituted 2-hydroxyphenylketones. This confirms the views of other workers (60,64) who have proposed that in strong sulphuric acid the central group in boron complexes is in the tetrahedral state and also that the complex formation reaction may involve both or either of the borate anion species $B(OH)(HSO_4)_3^-$ and $B(HSO_4)_4^-$ (64).

The apparent stability constants obtained from the n.m.r. work were lower than those obtained from fluorescence data and not as reproducible but were sufficiently close to the fluorescence values to validate the relative stabilities of the thoron and benzophenone complexes with boric acid.

The ^{11}B n.m.r. spectra of boric acid with mono or diazo derivatives of chromotropic acid confirmed the formation of the complexes with arsenazo I and arsenazo III which had been found in the earlier fluorescence investigation. Solutions containing boric acid and the monoazo-chromotropic acid derivatives chromotrope 2R or SPADNS also showed single n.m.r. peaks which could be attributed to a boric acid complex. The previously unreported boron complexes with the diazo derivatives sulphonazo III and carboxyarsenazo III, however, showed as two resonances in the n.m.r. spectra in contrast to that of arsenazo III where the spectrum contained only one (Figure 4.15). This may indicate that the more complex diazo derivatives are capable of forming complexes with the borate anion at more than one site such as the azo-hydroxy or the peri dihydroxy grouping.

5. CONCLUSIONS

5.1 Fluorimetric procedures for the determination of boron in steel using thoron.

Thoron had previously been shown to give fluorescence with boric acid (51) but had not previously been used in an analytical procedure involving the determination of boron in a metallic matrix. In this work thoron has been used in the development of a fluorimetric procedure for the direct determination of boron in the presence of iron giving a method for the analysis of boron in mild and low alloy steels equally suitable for routine batch work or for use as a reliable reference method.

The fluorescence intensity obtained using the proposed analytical procedure (appendix 1) was proportional to the boron content in the measured solution to greater than $0.30 mg l^{-1}$, equivalent to 0.020% boron in the solid steel. This covers the range of boron contents which produce the greatest effect on the hardenability of steel, 0.001 to 0.010% boron (2).

The limit of detection was governed by the magnitude and reproducibility of the fluorescence from blank solutions. Blank values were constant with the same batch of reagents and using the same apparatus. Using analytical grade reagents and ordinary glassware for the preparation of solutions, the resultant blank was of the order of 0.0005% boron, in contrast to most colorimetric procedures for boron where high background colours are usual. At this boron content the instrumental gain was such that no noise was apparent on the recorded trace. The limit of detection for the fluorimetric procedure may therefore be conservatively

estimated as less than 0.00005% boron, or 0.0008mgl^{-1} boron in the measured solution, based on twice the width of the pen line.

The reproducibility obtained using a steel with a certified boron content of 0.002% boron was ±0.0001% boron.

The proposed procedure has thus been shown to have a lower limit of detection and to provide more reproducible results than can be obtained with the British Standard method, a colorimetric procedure using curcumin (11). The attainable limit of detection was not as low as that provided by the most widely studied fluorimetric reagent for boron, HCMB, (0.0004mgl^{-1}) (41). However, the thoron - boric acid complex is formed without the heating period required with HCMB.

Optimum conditions for an analytical method are not determined by high sensitivity alone. It is important that moderate variations in conditions of complex formation should have as little effect as possible on the results obtained. In this respect the thoron fluorimetric procedure is much less influenced by small changes in experimental parameters than the colorimetric reaction with curcumin, which is noted for the requirement for stringent control of experimental conditions (9). The fluorescence produced by the thoron - boric acid complex was not markedly changed by moderate variations from the proposed concentration of sulphuric acid, thoron or iron in the measured solution. Fluorescence solutions prepared in 70 to 90% v/v sulphuric acid media gave relatively small resultant changes in fluorescent intensity. This is again in marked contrast to established

colorimetric procedures for boron in steel (9) in which only very small amounts of water can be tolerated, usually less than 10%.

Metal ions in the amounts commonly found in mild and low alloy steels caused no interference to the determination. At the higher levels encountered in alloy steels coloured ions caused variations in fluorescence intensity due to internal filter effects. The standardization of the British Chemical Standard sample 466/1, a stainless steel, for boron content (appendix 2) has shown that the use of appropriate blank and calibration solutions can overcome these effects. Titanium III reduces the thoron reagent and may completely decolourize it if present in sufficient amounts. The levels present in most steels (<1%) have little effect. Nitric and hydrochloric acids also decolourize the reagent and should be absent. No fluorescence was observed from solutions containing phosphoric or perchloric acids and their use must be avoided.

The formation of the fluorescent complex takes place in 90% v/v sulphuric acid solution but with proper precautions this need not cause any great practical difficulties. One of the aims of this project was to develop a procedure which did not require use of such a corrosive medium. This has not proved possible except in so much as the fluorescence from the thoron - boric acid complex can be developed over a much wider range of sulphuric acid concentrations than is applicable to colorimetric procedures employing acidic media. The use of almost concentrated sulphuric acid has, however, led to a very specific method for the determination of boron since a wide range of complexes formed

between thoron and metal ions do not survive in this highly acid medium.

The automated fluorescence procedure eliminates the problems associated with handling concentrated sulphuric acid and allows a more rapid determination as fluorescence can be reproducibly measured before equilibrium conditions are obtained. This enhances the suitability of the procedure for batch analysis.

The fluorimetric procedure is compatable with established dissolution techniques allowing conventional 'soluble' and 'insoluble' boron determinations to be made. This has an advantage over plasma techniques where dilute sulphuric acid is not an ideal solvent for the determination of boron in steel as the boron lines at 182.56 and 182.64 nm used in the ICP procedure are subject to spectral interference from sulphur at 182.62 nm.

Fluorimetric methods are capable of great sensitivity but have not achieved widespread use in the steel industry. The 150 nm Stokes' shift for the thoron - boric acid complex should, however, enable a satisfactory measurement to be made using a simple filter fluorimeter where the broad spectral band widths would compensate for any deficiency in the excitation source.

5.2 Formula and stability of the thoron - boric acid complex

No previous work has been reported on the complex formation between thoron and boric acid using conditions similar to those used in the fluorimetric procedure for the determination of boron in steel proposed in this work. The formula and apparent stability

constant of thoron - boric acid complex were accordingly investigated using a 90% v/v sulphuric acid medium and data obtained from fluorescence measurements.

The formula of the complex was determined by two independent procedures - the method of continuous variation (68) using a total reagent concentration of 10^{-5}M, and a mole ratio method (70), using a thoron concentration of 1.44×10^{-4}M. Both procedures gave results consistent with one molecule of thoron combining with one molecule of boric acid. The formula in 90% v/v sulphuric acid thus differs from that found in concentrated acid by Marcantonatos et al (51). Their work showed the complex to be composed of one molecule of thoron combined with two of boric acid when the total reagent concentration was 5×10^{-3}M.

The apparent stability constant of the thoron - boric acid complex was found to be $7.0 \times 10^{3}M^{-1}$ in 90% v/v sulphuric acid solutions containing 5×10^{-6}M thoron at a temperature of 25°C. Using this value of the apparent stability constant the amount of boric acid present as the thoron - boric acid complex at equilibrium under the conditions proposed for the analysis of boron in steel (appendix 1) is only 51%. Although the proportion of boric acid present as the complex can be increased by displacing the equilibrium concentrations with an increased excess of thoron this procedure is not useful analytically as the increased absorption of the resulting solution produces a decrease in the emitted fluorescence.

The stability constant is many magnitudes less than those of thoron - metal complexes ($\beta_1 = 1.4 \times 10^{10}M^{-2}$ for the thorium

complex (76)) but is comparable to those of other 1 : 1 boric acid complexes formed in sulphuric acid media of similar concentrations (10^3 to $10^5 M^{-1}$ (56-64)) suggesting that the boron atom has an environment in these complexes that is similar to that in the thoron - boric acid complex.

5.3 ^{11}B n.m.r. studies of the boric acid - thoron system in sulphuric acid media

^{11}B n.m.r. spectroscopy has been proposed as a suitable technique for quantitative determination and structural elucidation of boric acid esters in aqueous medium (85-87). However, no previous work has been reported on studies of boric acid in very acidic media. The present work has shown that ^{11}B n.m.r. can provide information on boric acid speciation, complex formation and stability in sulphuric acid solution, at concentrations where the low sensitivity of ^{13}C nmr would necessitate long data accumulation times and where ^{1}H spectra may not be sensitive to changes occurring at the boron species during complexation.

Low field (25.7MHz) ^{11}B n.m.r. spectra of boric acid in almost concentrated sulphuric acid showed two resonances with chemical shifts typical of tetrahedrally bonded boron species.

The sharp resonance at -3.4ppm decreased in intensity with decreasing sulphuric acid concentration. The constant relatively narrow line width (12Hz) of this peak indicated that it arose from a symmetrical boron species and is further evidence for assigning this resonance to the tetra(hydrogensulphato) borate anion proposed by Gillespie et al (78,79) as the form in which boric acid exists in solution in concentrated sulphuric acid.

The other broader peak moved down field from -2.4ppm with decreasing sulphuric acid concentration. The line width increased to 250Hz at intermediate sulphuric acid concentrations (around 60% v/v) and reduced to 50Hz as the acidity of the medium was further decreased (20% v/v). The change in chemical shift with sulphuric acid concentration is consistent with a corresponding variation in relative concentrations of tetrahedral borate anions and trigonal boric acid in a rapidly interconverting system. The variation of line width indicates the possible existence of several borate anions of the general formula $B(OH)_x(HSO_4)^-_{4-x}$. At the sulphuric acid concentration used in the fluorimetric work this borate anion may be taken as being predominantly $B(OH)(HSO_4)^-_3$, the species postulated by Marcantonatos et al (64) to account for an increase in rate of boron complex formulation with lowering of sulphuric acid concentration.

Although complex formation was apparent from the decrease in intensity of the $B(HSO_4)^-_4$ anion resonance when the n.m.r. spectra of thoron - boric acid solutions were recorded at 25.7MHz, the resolution was not sufficient for a separate resonance from the complex to be distinguished. 128MHz ^{11}B n.m.r. spectra of equimolar ($10^{-2}M$) thoron and boric acid solutions in 95% v/v sulphuric acid showed a well-resolved resonance attributable to the thoron - boric acid complex. The chemical shift of this resonance, -0.3ppm, indicates that the boron atom is also tetrahedrally bonded in the complex.

The ^{11}B n.m.r. spectra of boric acid and a range of 2-hydroxyphenylketones and of some phenylazo derivatives of chromotropic acid showed the presence of boric acid complex

having similar chemical shifts to that of the thoron - boric acid complex confirming suggestions that at high sulphuric acid concentrations the central group in boron complexes is in a tetrahedral state (60,64). The complexes observed with the di(phenylazo) derivatives of chromotropic acid, sulphonazo III, carboxyarsenazo III and arsenazo III do not appear to have been previously reported.

Apparent stability constants calculated from n.m.r. data have confirmed the relative stabilities of the thoron and HCMB boric acid complexes obtained from fluorimetric measurements.

The apparent stability constant of the thoron - boric acid complex determined from ^{11}B n.m.r. measurements was found to decrease rapidly with sulphuric acid concentrations less than 70% v/v (as did the fluorescence intensity). The tetrahedral character of the hydroxylated borate anion, as shown by the chemical shift of the resonance, also decreases rapidly below 70% v/v sulphuric acid. The variation in stability of the complex with sulphuric acid concentration may however depend to a greater extent on the degree of protonation of the organic ligand.

5.4 Proposal for mechanism of formation of the thoron - boric acid complex

In concentrated acid media thoron, together with mono and diazophenylchromotropic acid derivatives, are protonated on the azo group (94) with accompanying bathochromic shifts and hyperchromic effects on their electronic spectra. The nature of the hydrogen-nitrogen bonds formed as a result of the protonation process is not well established. It has been proposed (95) that

the protonated structure can be characterized by a 'tautomeric equilibrium' (strictly a resonance condition) which for thoron would be as shown in Figure 5.1 I and II where for the azo form,I, the site of protonation is the nitrogen next to the phenyl group. Other proposals (96) invoke non localized hydrogen-azo bonds with the formal change 'randomly located' on the azo group. Structures III and IV in Figure 5.1 are the corresponding forms for thoron. The reagent would be present as the trans isomeric form which is stabilized by the effect of intramolecular hydrogen bonds between the hydroxy and azo groups, with the quinone-hydrazone form IV, predominant at high sulphuric acid concentration, being responsible for the observed bathochromic shift.

The bulky non planar arsonic acid grouping ortho to the azo group exerts a strong negative induction effect and reduces the basicity of the reagent so that protonation takes place only in strongly acidic media (97). The reaction between the borate anions and the protonated thoron should be regarded as not leading to a radical change in the conjugated system of the thoron molecule as no shift or broadening of the absorption bond in its electronic spectrum was apparent on complex formation. The proposed scheme, illustrated in Figure 5.2, is the simplest reaction mechanism for the formation of the thoron - boric acid complex in sulphuric acid media of high concentration which is in accordance with all the experimental evidence. In this scheme the complexed boron atom is tetrahedrally bound and is part of a six-membered ring. This configuration is supported by the ^{11}B n.m.r. chemical shift of the complex as it has been shown (85) that a boron atom which is a member of a five-membered ring would have a chemical shift

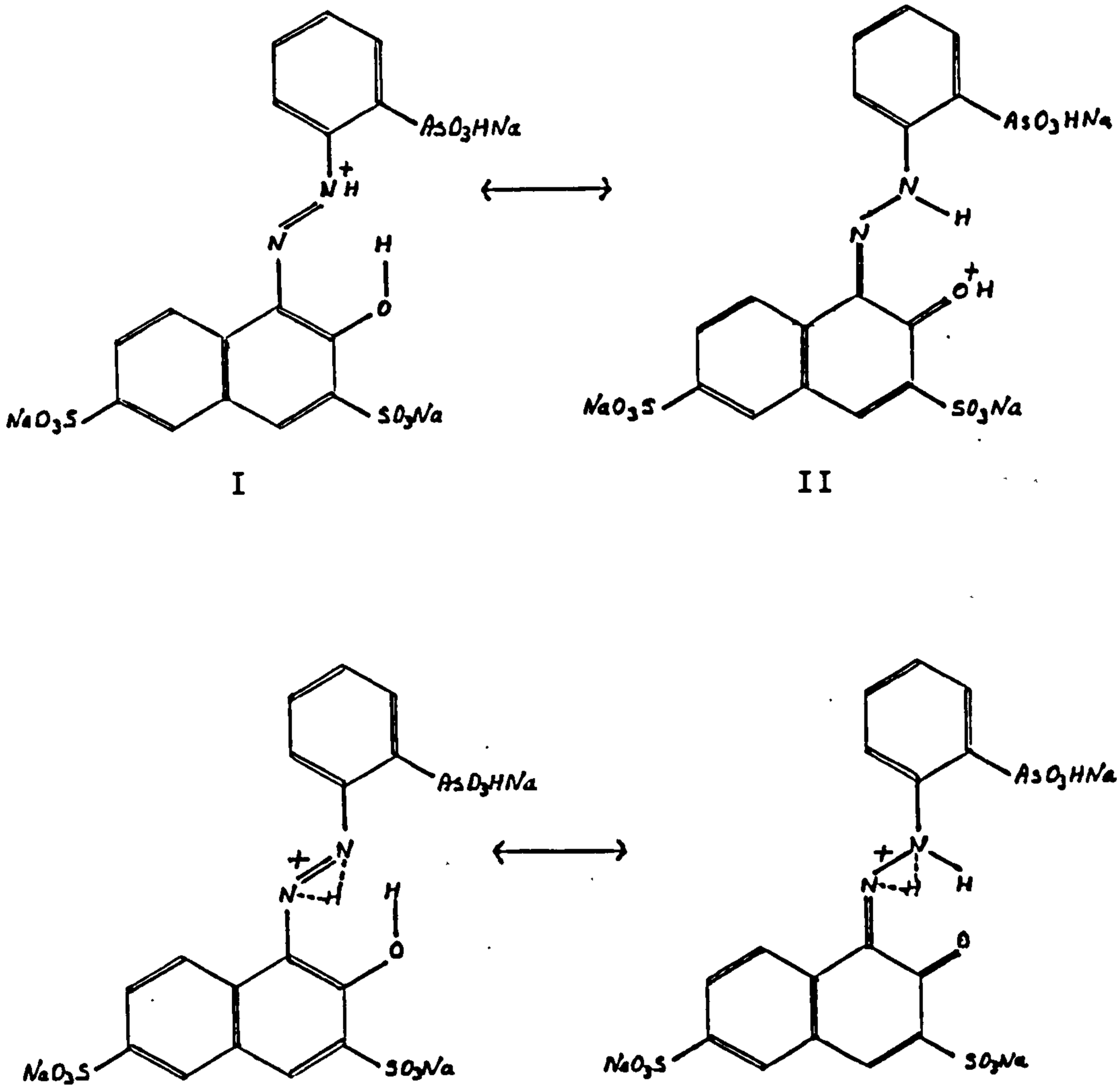


FIGURE 5.1 STRUCTURES FOR PROTONATED THORON

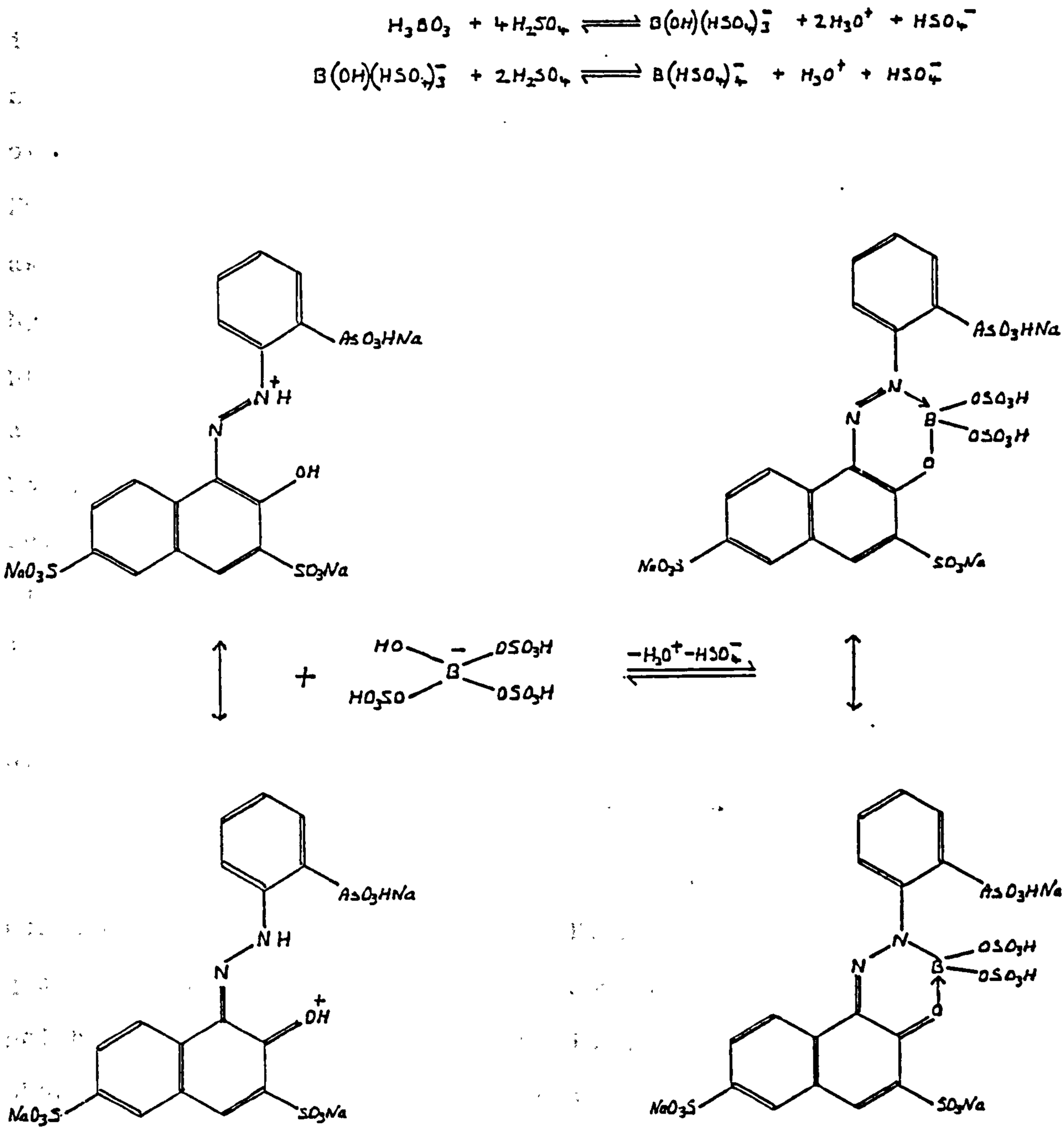


FIGURE 5.2 PROPOSED REACTION MECHANISM FOR FORMATION OF THORON-BORIC ACID COMPLEX

5 to 10ppm to lower field than the observed value for the thoron - boric acid complex.

Kinetic studies on boric acid esterification (98) and complex formation (64) have confirmed that a single step reaction scheme is an oversimplification and it is reasonable to assume a steady state concentration of an intermediate species since in the overall reaction at least two bonds are made and two broken. For thoron - boric acid complexation the intermediate would be as shown in Figure 5.3. The ring closure would then entail hydrogen sulphato anion displacement followed by the loss of a proton. The ring opening mechanism would be inititated by proton attack at the negative polar site of the complex giving a trigonal boron atom which is rapidly coordinated by a hydrogen sulphato anion. The ring closure should be favoured by the stabilizing effects of the six-membered ring. The ring closure scheme is illustrated in Figure 5.4.

5.5 Formation of boric acid complexes with phenyl azo chromotropic acids

The complex formed by chromotropic acid and boric acid is considered to be of the form I in Figure 5.5. (99) based on the generally accepted structures for complexes of boric acid with polyhydroxy compounds. In sulphuric acid media this work has shown that boron would be present as hydrogen sulphato borate anions. A complex of the structure II in Figure 5.5 would be more probable, although neither trigonal nor tetrahedral boron complexed species were found in the ^{11}B n.m.r. spectra of the chromotropic acid - boric acid solutions when complexation was

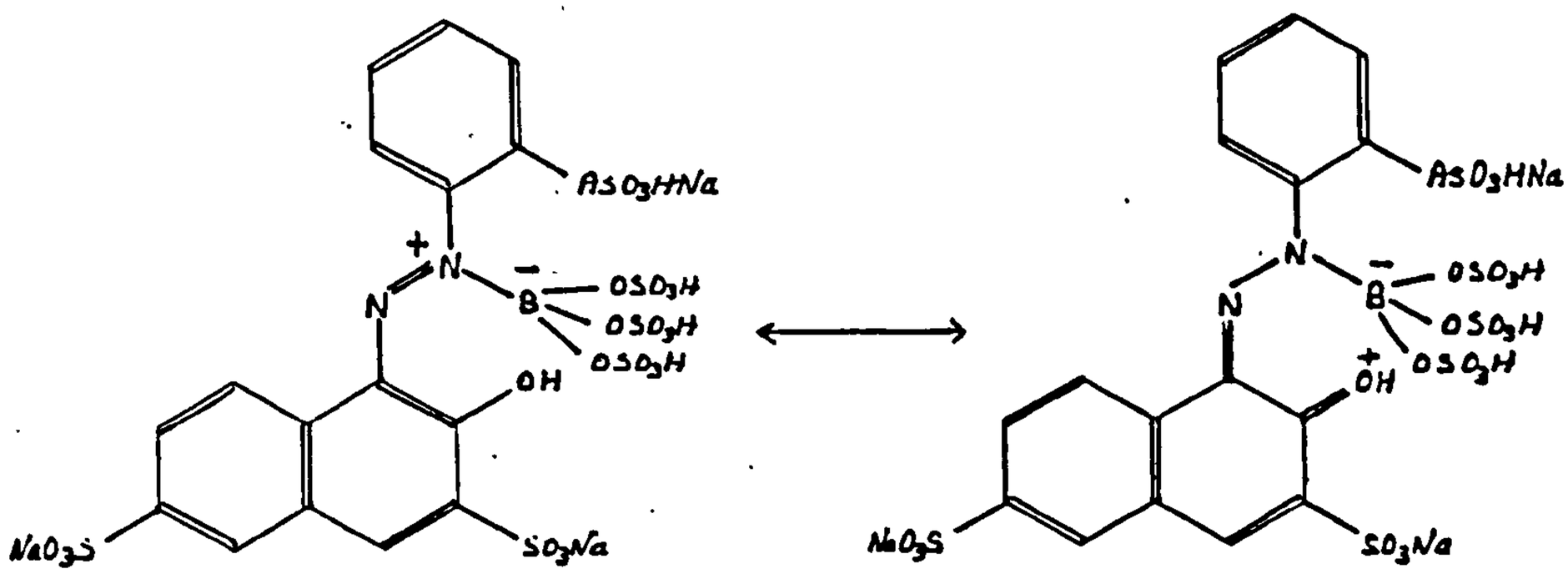


FIGURE 5.3 POSSIBLE INTERMEDIATE SPECIES

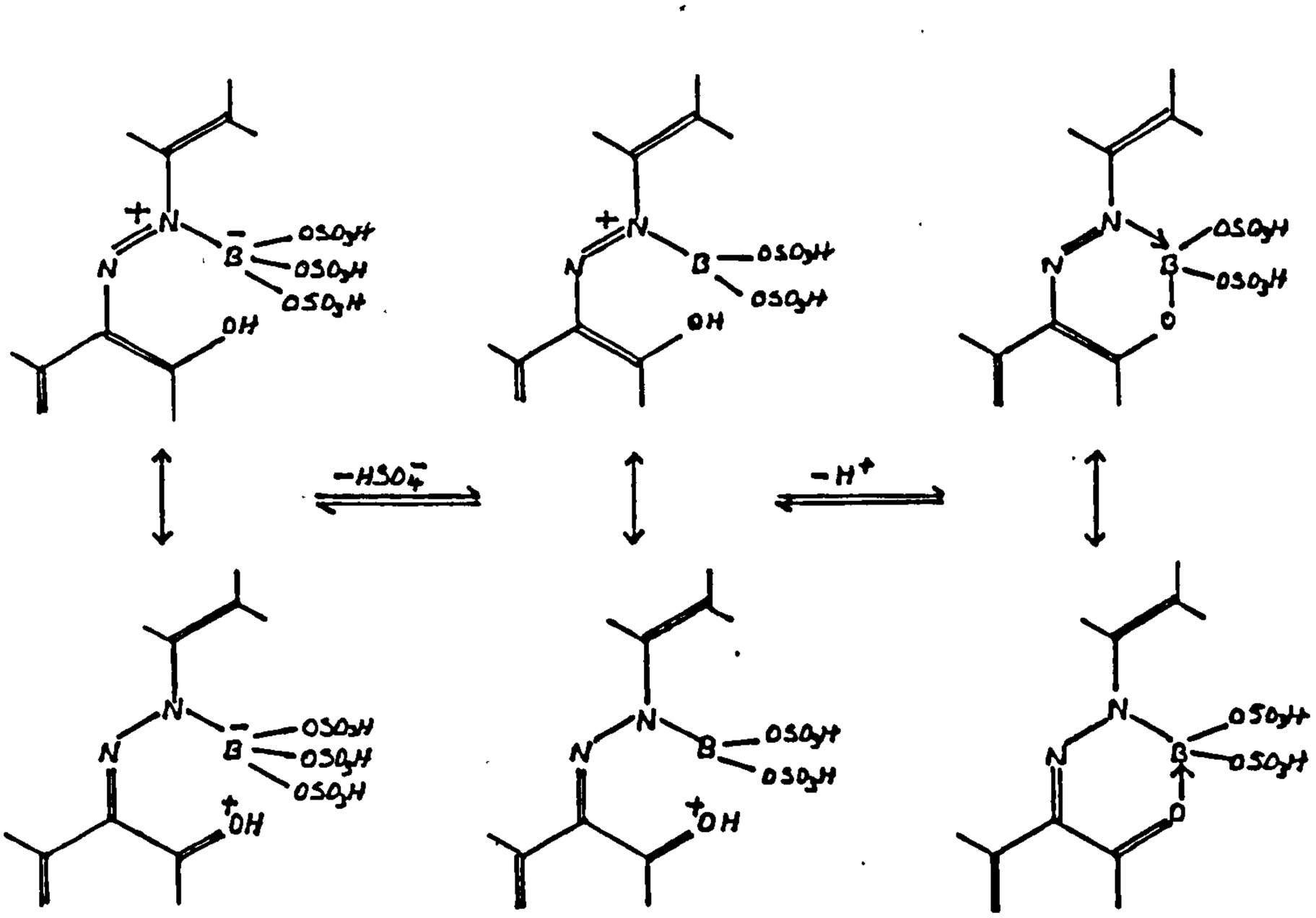
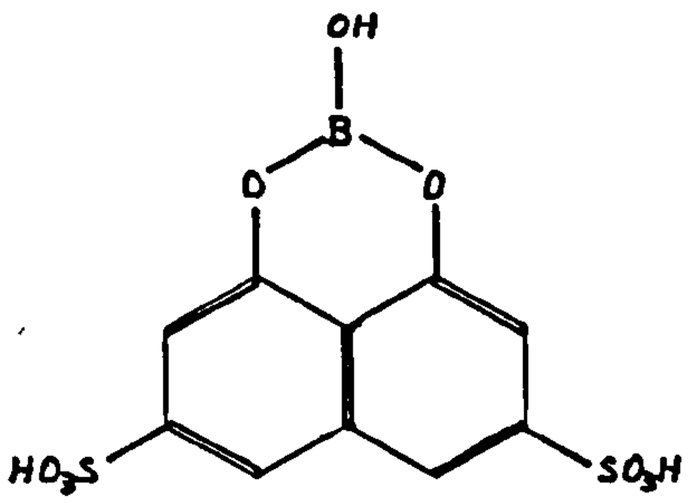
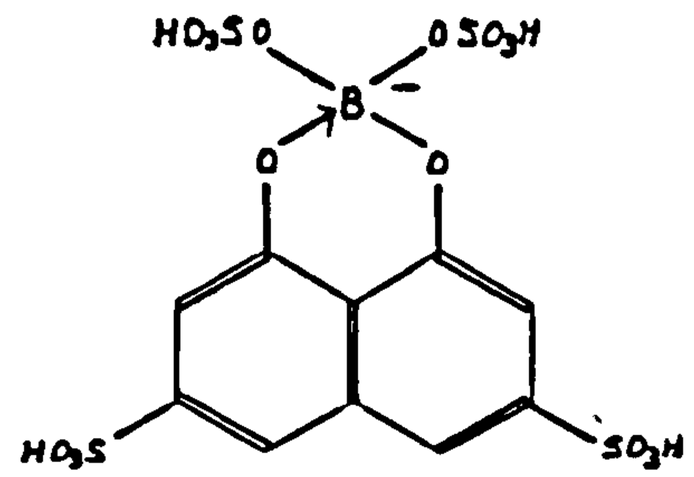


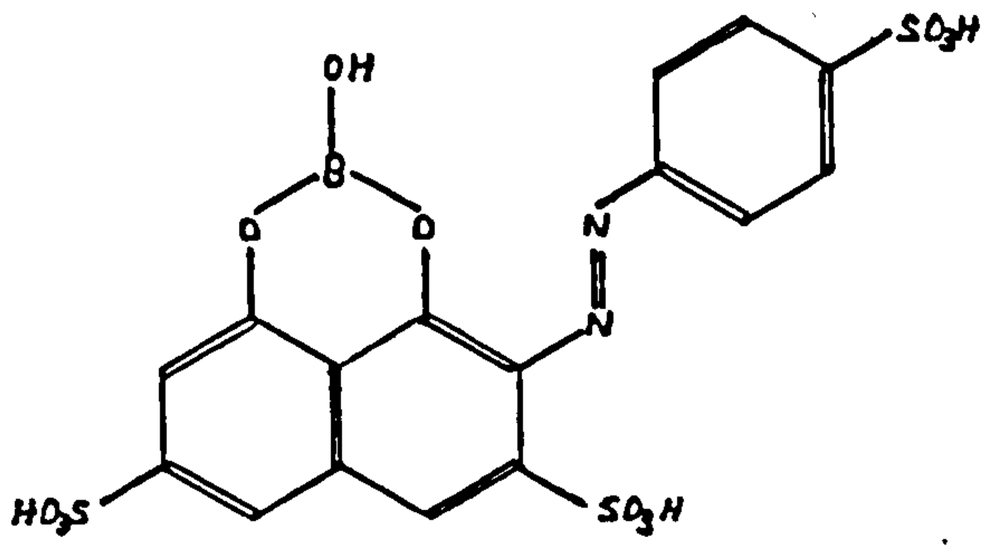
FIGURE 5.4 PROPOSED RING CLOSURE MECHANISM
(ONLY REACTIVE CENTRES SHOWN)



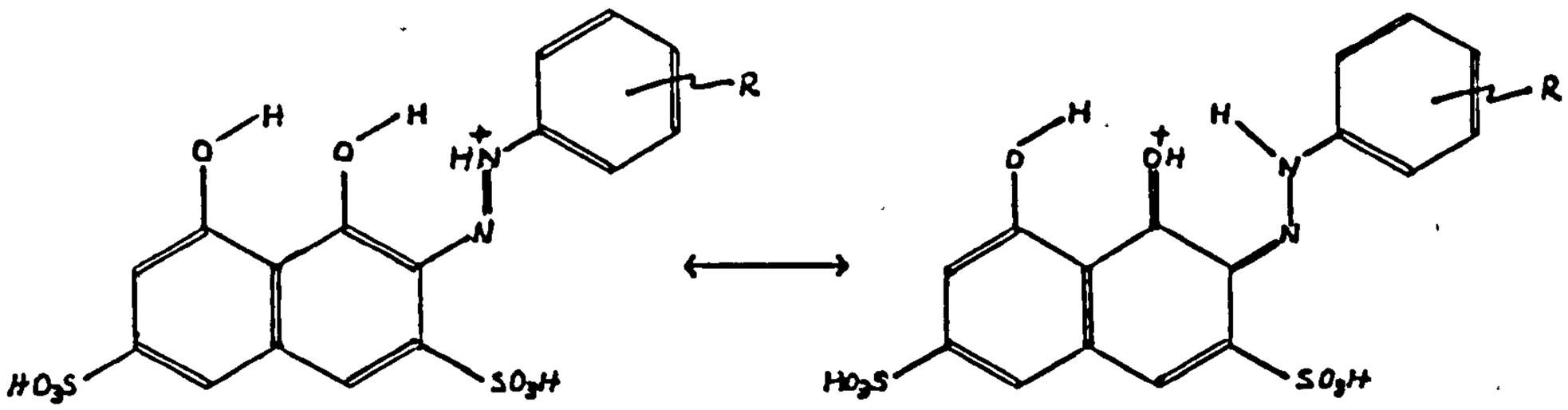
I



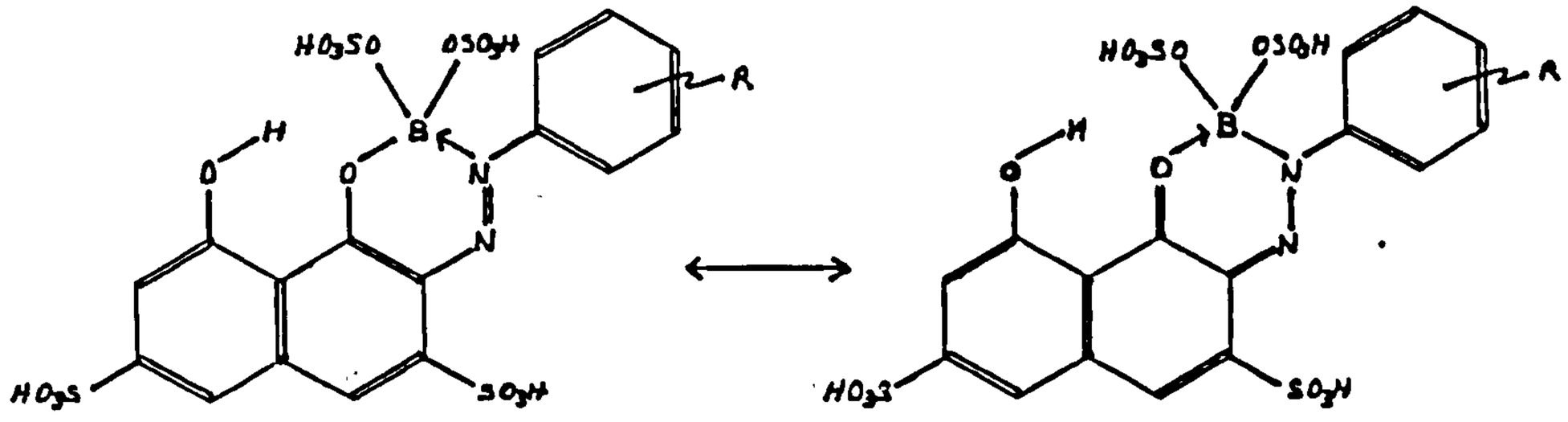
II



III



IV



V

FIGURE 5.5

indicated only by reduction in intensity of uncomplexed borate anion resonances, possibly the result of rapid exchange of boron species.

Complexes of mono and diphenylazo chromotropic acid derivatives with elements which do not form π bonds are usually considered to be similar in form to that of chromotropic acid, the reaction taking place with the *peri* hydroxy groups of the ligand (100). The coloured SPADNS - boric acid complex (Figure 5.5 III) formed in concentrated sulphuric acid has been assumed to have this structure (89).

The data obtained from ^{11}Bn.m.r. spectra of the boric acid complexes with the monophenylazo chromotropic acid derivatives chromotrope 2R, SPADNS and arsenazo I were very similar to the results obtained for the thoron complex and clearly show that they all contain tetrahedral boron species. Taken with the known ability of these ligands to give rise to resonating structures shown as IV in Figure 5.5 (94), which are similar to those proposed for thoron, it is feasible that the boric acid complexes with monophenylazo chromotropic acid derivatives are formed by the same reaction mechanism that is proposed for the thoron - boric acid complex giving complexes of the form V in Figure 5.5.

Of the previously unreported boric acid complexes with diphenylazo chromotropic acid derivatives, the ^{11}B n.m.r. spectra of sulphonazo III and carboxyarsenazo III showed two resonances associated with boric acid complexes while that of arsenazo III showed one. Muk and Savvin (97) have shown that the bulky arsonic acid groups of arsenazo III bound to the phenyl groups σ, σ' to

the azo groups, cause the structure of the molecule to be considerably distorted from the essentially planar form of other 2, 2' substituted diphenylazo chromotropic acids. This results in the electronic structure of arsenazo III more closely resembling that of arsenazo I with only one of the two azo groups being protonated in strong acids and is in accord with the formation of a single boric acid complex with the resultant single ^{11}B n.m.r. resonance.

The two ^{11}B n.m.r. resonances obtained with the sulphonazo III and carboxyarsenazo III boric acid systems indicate bifunctionality of the ligand with complexes being formed with the borate anion at more than one site such as the azo - hydroxy or the *peri* hydroxy groupings.

5.6 Possible further work

(a) An investigation of the effect of a wider range of metallic ions on the fluorimetric determination of the thoron - boron acid complex would enable an assessment to be made of the possibility of applying the procedure to the determination of boron in other metals.

(b) The determination of the formula of the thoron - boron acid complex over a wider range of conditions may establish whether there is a clear cut transition to the formation of the 1 : 2 thoron : boric acid complex reported by Marcantonatos (51).

(c) A kinetic investigation of the formation of the thoron - boric acid complex would provide further information on the reaction

mechanism. The existance or otherwise of a steady state intermediate could be established. An investigation of the variation of rate of complex formation with sulphuric acid concentration would enable a comparison to be made with other ligand systems, such as carmine - boric acid or HCMB - boric acid, where the rate increases with a decrease in sulphuric acid concentration.

(d) The examination of boric acid complexes with the 2'-carboxyphenylazo and 2'-sulphophenylazo analogues of thoron for fluorescent complex formation and for complex stability would provide a better understanding of the role of the arsonic acid grouping in the thoron - boric acid complex. The expected larger protonation constants of these ligands may enable complex formation in less concentrated sulphuric acid than is the case with thoron.

APPENDIX 1 PROCEDURE FOR THE DETERMINATION OF BORON IN STEEL

APPENDIX 1 PROCEDURE FOR THE FLUORIMETRIC DETERMINATION OF BORON IN STEEL USING THORON

A1.1 Reagents

Sulphuric acid Analar sg 1.84	
Sulphuric acid, 30% v/v	To 600ml of distilled water add 300ml of sulphuric acid AR sg 1.84 . Cool. Make up to 1 litre.
Sodium carbonate Analar	
Thoron, 0.09% in sulphuric acid.	Dissolve 0.09g of thoron (1-(2'-arseno-phenylazo)-2-hydroxynaphthalene-3,6-disulphonic acid tri sodium salt) in sulphuric acid AR sg 1.84. Make up to 100ml with sulphuric acid.
Boric acid solution, ($20mgl^{-1}B$)	Dissolve 0.1144g of boric acid Analar in sulphuric acid, 30% v/v. Make up to 1 litre with sulphuric acid, 30% v/v.
High purity iron	BCS 260/4 (boron content <.0001%)

A1.2 Dissolution

Transfer 1.0g of sample to a soda glass boiling tube. Add 40ml of sulphuric acid (30% v/v). Insert an air condenser and heat in a water bath at about 80°C until solvent action ceases. Cool, disconnect and rinse the condenser with a little sulphuric acid (30% v/v). Filter through a small filter paper (No.540) previously washed with sulphuric acid (30% v/v) and collect the

filtrate in a 100ml volumetric flask. Wash the paper with the minimum amount of sulphuric acid (30% v/v). Reserve the filtrate.

Wash the paper acid free and transfer to a small platinum crucible. Sprinkle 0.2g of sodium carbonate over the paper, dry and ignite at a low temperature until carbonaceous matter is removed. Add a further 0.8g of sodium carbonate and fuse at 1100°C for 15 minutes. Cool, dissolve the fused mass by additions of sulphuric acid (30% v/v) and add to the reserved filtrate. Dilute to 100ml with sulphuric acid (30% v/v) and mix.

A1.3 Fluorimetric Procedure

a) Manual Procedure

Transfer a 15ml aliquot of the sample solution to a 100ml beaker. Add 10ml of thoron solution (0.09% w/v in sulphuric acid) with cooling. Transfer to a 100ml volumetric flask. Wash beaker with 75ml of sulphuric acid(sg 1.84). Add to flask and when cool make up to 100ml with sulphuric acid (sg 1.84).

Measure the fluorescence after sufficient time has elapsed for maximum fluorescence to develop (90 mins).

Prepare a reagent blank concurrently.

Using the Perkin-Elmer-Hitachi MPF 2A spectrofluorimeter with a 1cm silica cell the following conditions were employed.

Entrance slits 18 nm Exit slits 12 nm

Excitation wavelength 420 nm Emission wavelength 580 nm

Sensitivity range 2 Ratio sensitivity range 2.

Obtain the boron content by reference to a calibration graph prepared from synthetic or BCS steels.

b) Automated Procedure using an Auto Analyzer

Set up the automated flow system as shown in the diagram (Figure 2.29). Pass the sample solutions through the system at a speed of 20 samples per hour. The fluorimeter settings are as the manual procedure.

A1.3 Calibration

To six 1.0g samples of boron free iron add respectively 0,1.0,2.0,3.0,4.0 and 5.0ml of standard boron solution ($20mgl^{-1}$ boron in sulphuric acid (30% v/v)) and carry out the described dissolution, omitting the fusion, to give solutions equivalent to 0,.002,.004,.006,.008 and .010% boron in steel.

APPENDIX 2 CERTIFICATE FOR THE ANALYSIS OF STAINLESS STEEL (INCLUDING BORON CONTENT)

MAIN EDITION

BUREAU OF ANALYSED SAMPLES LTD.

Directors (1979-86):-
P.D. RIDSDALE, *B.Sc., C.Eng., M.I.M.*, (Managing)
B. BAGSHAWE, *A.Met., C.Eng., F.I.M.*
R.P. MEERES, *B.A.*, (Oxon)
W.F. WILSON

BRITISH CHEMICAL STANDARD CERTIFIED REFERENCE MATERIAL

CERTIFICATE OF ANALYSIS
BCS*/SS†-CRM No. 466/1
AUSTENITIC STAINLESS STEEL

Prepared under rigorous laboratory conditions and, AFTER STANDARDIZATION BY ANALYSTS IN GREAT BRITAIN, issued by the Bureau of Analysed Samples Ltd.

The Material for this CRM was specially cast by Firth Vickers Foundry Ltd., and was forged and rolled by Sheffield Forgemasters Ltd.

ANALYSES

Mean of 4 values — mass content in %

Analyst No.	C	Si (Total)	Mn	P	S	Cr	Mo	Ni	As	B	Nb	Pb	Sn	Ta
1	0.063	0.509	0.698	0.021	0.016	17.65	2.19	8.64	0.018	0.0025	0.032	0.0014	0.0053	*0.0002*
2	0.066	0.490	0.700	0.020	0.016	17.64	2.21	8.58	-	-	-	-	-	-
3	0.064	0.507	0.692	0.020	0.015	17.66	2.20	8.56	0.016	-	-	0.0018	-	-
4	0.060	0.504	0.704	0.019	0.014	17.62	2.18	8.56	0.017	0.0022	0.030	0.0014	0.0046	*0.0004*
5	0.060	0.510	0.684	0.020	0.016	17.62	2.18	8.66	0.016	-	0.032	0.0014	0.0048	*0.0005*
6	0.063	0.505	0.710	0.020	0.017	17.66	2.21	8.58	-	0.0022	0.025	0.0015	0.0056	-
7	0.061	0.504	0.700	0.020	0.016	17.65	2.18	8.64	-	-	-	-	-	-
8	0.062	-	-	0.021	0.018	17.75	2.19	8.57	0.020	0.0025	0.028	0.0012	0.0048	*0.0002*
9	-	0.514	0.700	-	-	17.62	-	8.64	-	-	-	-	-	-
10	-	-	-	-	-	-	-	8.64	-	0.0027	-	-	-	-
M_M	**0.062**	**0.505**	**0.698**	**0.020**	**0.016**	**17.65**	**2.19**	**8.61**	**0.017**	**0.0024**	**0.029**	**0.0014**	**0.0050**	*0.0003*
s_M	0.002	0.007	0.008	0.001	0.001	0.04	0.01	0.04	0.002	0.0002	0.003	0.0002	0.0004	-

M_M: Mean of the intralaboratory means. s_M: Standard deviation of the intralaboratory means.

The above figures are those which each analyst has decided upon after careful verification
Figures in bold type certified, figures in small italic type only approximate.

*British Chemical Standard — chips graded 1700-250µm (10-60 mesh) for chemical analysis

† Spectroscopic Standard — discs 38 mm x 19 mm thick for spectroscopic analysis

Note: Due to slight segregation of certain elements an area 6mm in diameter in the centre of the disc samples should be avoided for emission spectrometry.

CO-OPERATING ANALYSTS AND FIRMS

INDEPENDENT ANALYSTS

1. DONNELLY, D., *M.Sc.*, *C.Chem.*, *M.R.S.C.*, Round Oak Laboratories Ltd., Brierley Hill.

2. HASTINGS, J.C., The Sheffield Testing Works Ltd., Sheffield.

3. KATZ, A.M., Alfred H. Knight International Ltd., Wallasey.

4. PAGE-GIBSON, J.E., *B.Sc.*, *C.Chem.*, *M.R.S.C.*, Ridsdale and Co. Ltd., Middlesbrough.

5. PICKERING, J.L., *C.Chem.*, *M.R.S.C.*, Messrs Sandberg, London.

GOVERNMENT DEPARTMENTS

6. NICHOLLS, H.A., *C.Chem.*, *F.R.S.C.*, Bragg Laboratory, Materials Quality Assurance Directorate, Sheffield

ANALYSTS representing MAKERS and USERS

7. DOUGHTY, A., APV Paramount Ltd., Crawley.

8. KIRKBY, C.I., *B.Sc.*, and HANCOCK, R., Stocksbridge and Tinsley Park Works, Sheffield.

9. WISE, R.A., Bonar Langley Alloys Ltd., Slough.

10. DOUGHTY, W., BSC Rotherham Works, Rotherham.

BCS/SS-CRM No. 466/1
AUSTENITIC STAINLESS STEEL

NOTES ON METHODS USED

CARBON

Analysts Nos. 1, 2, 3, 6, and 8 determined carbon by high frequency combustion/infrared absorption. Nos. 4, 5 and 7 used non-aqueous titration according to the British Standard Carbon Method 4*.

SILICON

All analysts determined silicon gravimetrically by dehydration with perchloric acid, according to the British Standard Silicon Method 1*.

MANGANESE

Analysts Nos. 1 and 5 determined manganese by FAAS. Nos. 2 and 9 determined manganese titrimetrically after a zinc oxide separation according to the British Standard Manganese Method 1*. The remaining analysts used photometric methods, Nos. 3, 4 and 6 after oxidation with potassium periodate according to the British Standard Manganese Method 2*, No. 7 after oxidation with ammonium persulphate/silver nitrate.

PHOSPHORUS

All analysts except No. 2 determined phosphorus photometrically as phosphovanadomolybdate according to the British Standard Phosphorus Method 2*. No. 2 used a titrimetric method after separation as phosphomolybdate.

SULPHUR

Analysts Nos. 1, 2, 3, 5, 6 and 8 determined sulphur by combustion methods. All except No. 5 used high frequency combustion/infrared absorption. No. 5 absorbed in hydrogen peroxide and titrated with borate. Nos. 4 and 7 determined sulphur gravimetrically according to the British Standard Sulphur Method 1*.

CHROMIUM

All analysts determined chromium by titration with ammonium ferrous sulphate after oxidation with ammonium persulphate/silver nitrate. All except No. 5 used the British Standard Chromium Method 1*. No. 5 used the Analoid Method No. 37.

MOLYBDENUM

Analysts Nos. 1 and 3 determined molybdenum using FAAS. All other analysts determined molybdenum photometrically as oxythiocyanate, Nos. 2, 4, 7 and 8 according to the British Standard Molybdenum Method 1*, Nos. 5 and 6 according to Analoid Method No. 42.

NICKEL

Analyst No.1 determined nickel using FAAS. Nos. 2, 3, 4, 5 and 8 determined nickel by titration after separation with dimethylglyoxime. Nos. 2 and 3 titrated with potassium cyanide solution according to the British Standard Nickel Method 1*. Nos. 4 and 5 dissolved the precipitate in dilute sulphuric acid, boiled with excess of ferric sulphate and titrated with dichromate solution (Analoid Method No. 62). No. 8 titrated with EDTA. Nos. 6 and 7 used dimethylglyoxime photometric methods. Nos. 9 and 10 determined nickel gravimetrically with dimethylglyoxime.

ARSENIC

Analysts Nos. 1, 3 and 4 determined arsenic photometrically with silver diethyldithiocarbamate after separation of arsenic as arsine by reduction with zinc. Nos 5 and 8 determined arsenic photometrically as molybdenum blue. No. 5 extracted the arsenic as iodide into chloroform (Fogg et al., Analyst, 1972, 97, 657) and No. 8 as chloride (Nall, Analyst, 1971, 65, 398).

BORON

All analysts determined boron photometrically; Nos. 1, 6, 8 and 10 with curcumin and No. 4 with dianthrimide.

Analyst No.1 also determined boron fluorimetrically with Thoron and obtained a mean value of 0.0025%. Analyst No. 6 also determined boron by ICP-AES and obtained a value of 0.0020%.

NIOBIUM

Analysts. Nos. 1, 4, 5 and 8 determined niobium photometrically with PAR after separation with phenylarsonic acid. No. 6 extracted niobium as thiocyanate into acidified acetone and completed photometrically according to the British Standard Niobium Method 1*.

LEAD

Analysts Nos. 1, 3, 4, 5 and 6 determined lead by AAS. No. 3 separated lead by extraction with sodium diethyldithiocarbamate into 4-methylpentan-2-one. Nos. 4 and 5 separated lead as the iodide with a solution of TOPO in 4-methylpentan-2-one. Nos. 4 and 6 completed using ETA-AAS. No. 8 determined lead photometrically with dithizone according to the British Standard Lead Method 3*.

TIN

Analysts Nos. 1, 5 and 6 determined tin using FAAS. No. 5 separated tin as the iodide with a solution of TOPO in 4-methylpentan-2-one. No. 4 used ETA-AAS. No. 8. determined tin titrimetrically after separation as sulphide according to the British Standard Tin Method 1*.

TANTALUM

All analysts determined tantalum photometrically according to the British Standard Tantalum Method 1*.

Abbreviations

ETA-AAS : Electrothermal atomisation-atomic absorption spectrometry
FAAS : Flame atomic absorption spectrometry
ICP-AES : Inductively coupled plasma - atomic emission spectrometry
TOPO : Tri-octyl phosphine oxide
PAR : 4-(2-Pyridylazo) - resorcinol

*Methods for Sampling and Analysis of Iron, Steel and Other Ferrous Metals, B.S. Handbook No. 19, first published 1970 by the British Standards Institution, 2 Park Street, London, W1A 2BS.

NEWHAM HALL,
MIDDLESBROUGH
ENGLAND.

For BUREAU OF ANALYSED SAMPLES LTD.
P.D. RIDSDALE,
Managing Director

Preliminary Edition ..... September 1984
Main Edition ..... April 1986

APPENDIX 3 DATA FOR DETERMINATION OF APPARENT STABILITY CONSTANT OF THORON-BORIC ACID COMPLEX

FIGURE A.3.1 DETERMINATION OF APPARENT STABILITY CONSTANT

THORON CONC. $B_o = 5 \times 10^{-6}$M SULPHURIC ACID 90% v/v

BORIC ACID CONC. $A_o = 10^{-4}$ TO 10^{-3}M TEMPERATURE 25°C

A_o /10^{-4}M	$\frac{1}{A_o}$ /$10^{3}M^{-1}$	EXCITATION 420 nm		EXCITATION 486 nm	
		INTENSITY I_f	$\frac{B_o}{I_f}$/10^{-6}M	INTENSITY I_f	$\frac{B_o}{I_f}$/10^{-6}M
SERIES I					
1	10.0	15.8	31.65	31.6	15.82
2	5.0	21.0	23.80	43.0	11.63
3	3.33	28.2	17.73	54.7	9.14
4	2.5	27.4	18.25	55.0	9.09
5	2.0	28.7	17.42	55.8	8.50
6	1.66	29.6	16.89	60.0	8.33
7	1.43	31.3	15.97	62.6	7.99
8	1.25	32.0	15.62	64.4	7.76
9	1.11	32.9	15.20	65.5	7.63
10	1.0	32.2	15.53	64.7	7.73
SERIES II					
1	10.0	17.6	28.41	37.5	13.33
1.1	9.09	18.9	26.46	38.8	12.89
1.25	8.0	-	-	41.9	11.93
1.4	7.14	20.6	24.27	44.0	11.36
1.7	5.88	23.2	21.55	48.5	10.31
2.0	5.00	-	-	52.5	9.52
2.2	4.55	25.8	19.38	54.4	9.17
2.5	4.0	27.0	18.52	57.1	8.76
2.85	3.51	28.7	17.42	59.4	8.42
3.3	3.03	29.4	17.01	61.9	8.08
4.0	2.50	30.5	16.39	64.7	7.73
5.0	2.0	32.7	15.29	68.9	7.26
6.25	1.6	34.5	14.49	72.6	6.89
8.3	1.20	36.5	13.70	75.5	6.62
10.0	1.0	37.1	13.48	78.9	6.34

FLUORESCENCE INTENSITY I_f = PEAK HEIGHT CORRECTED FOR BLANK FLUORESCENCE

FIGURE A3.2 DETERMINATION OF STABILITY CONSTANT OF THORON - BORIC ACID COMPLEX
SERIES I λ EXCITATION 420 nm

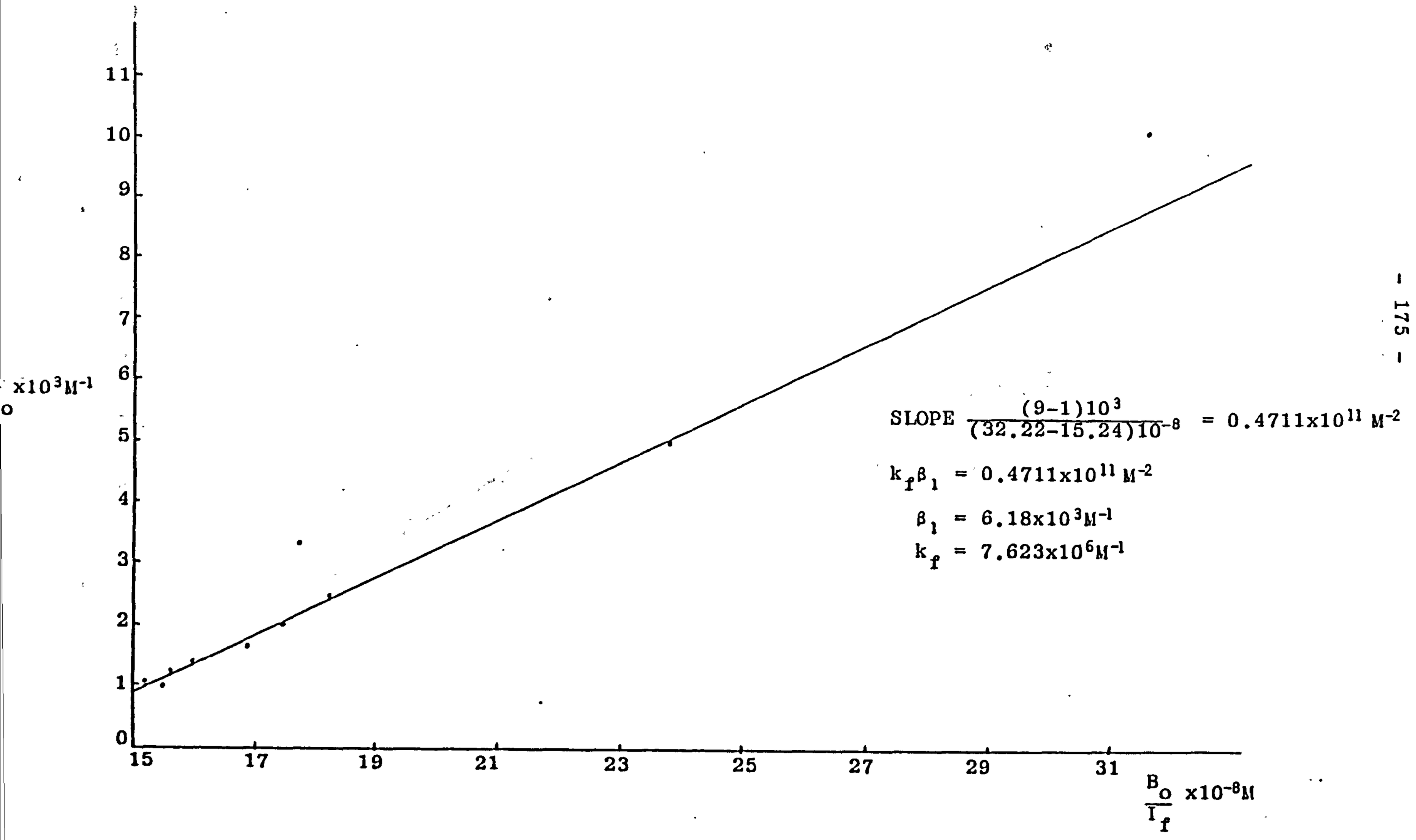
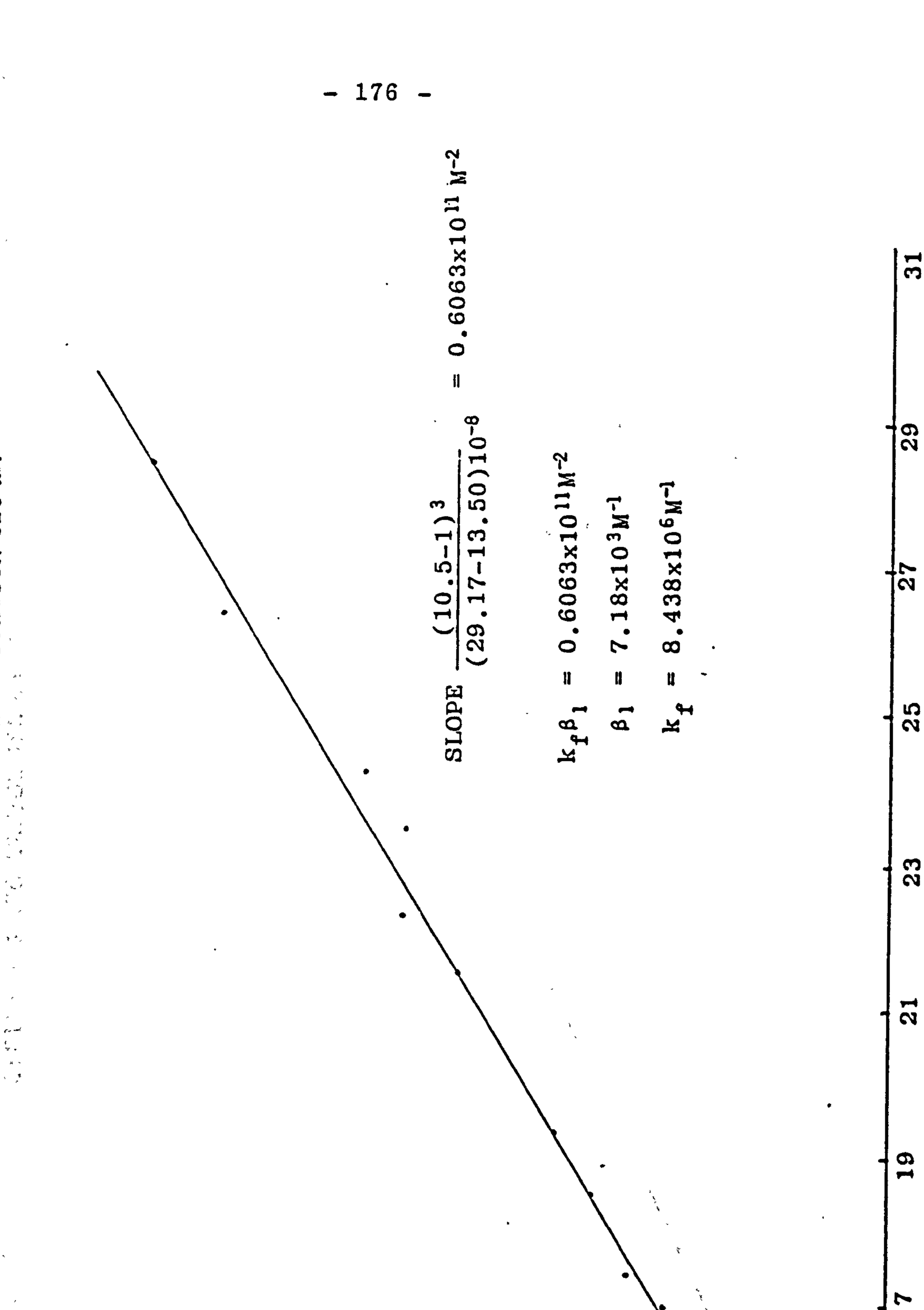


FIGURE A3.3 DETERMINATION OF STABILITY CONSTANT OF THORON – BORIC ACID COMPLEX
SERIES II λ EXCITATION 420 nm



$$\text{SLOPE} \frac{(10.5-1)^3}{(29.17-13.50)10^{-8}} = 0.6063\times10^{11}\ M^{-2}$$

$$k_f\beta_1 = 0.6063\times10^{11} M^{-2}$$

$$\beta_1 = 7.18\times10^3 M^{-1}$$

$$k_f = 8.438\times10^6 M^{-1}$$

FIGURE A3.4 DETERMINATION OF STABILITY CONSTANT OF THORON – BORIC ACID COMPLEX
SERIES I λ EXCITATION 486 nm

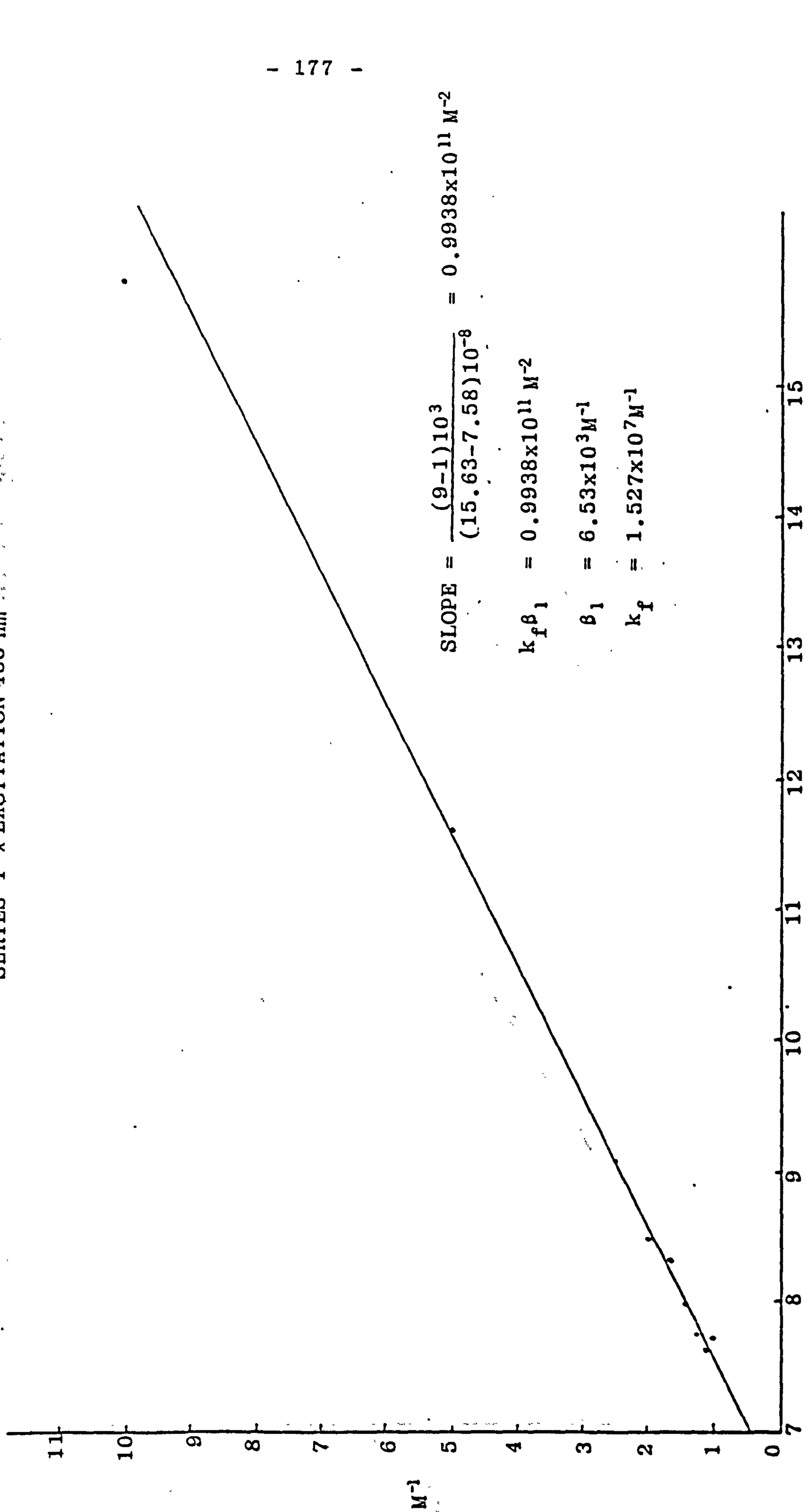
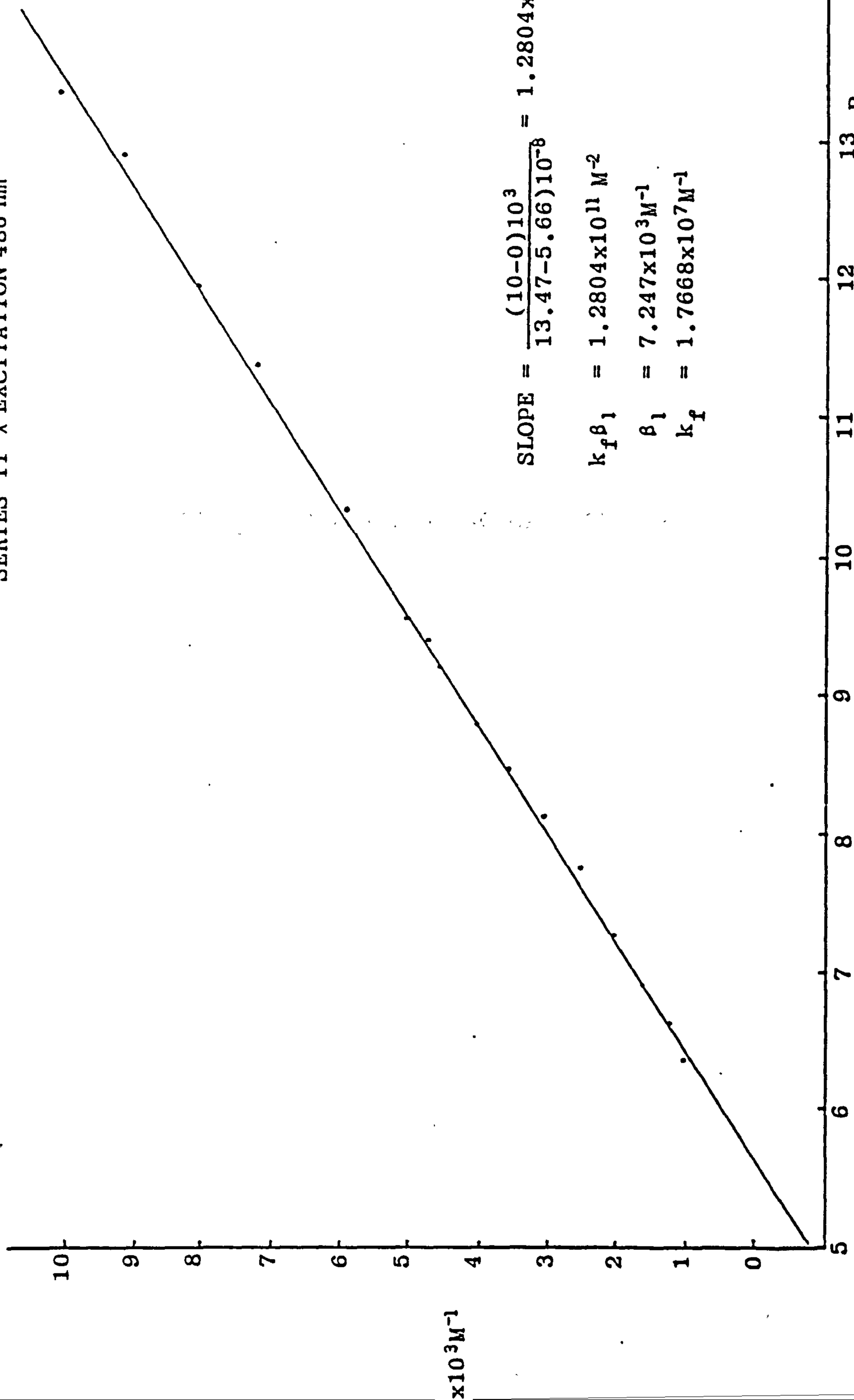


FIGURE A3.5 DETERMINATION OF STABILITY CONSTANT OF THORON – BORON ACID COMPLEX
SERIES II λ EXCITATION 486 nm



APPENDIX 4 CONVERSION FACTORS FOR MPF 2A

APPENDIX 4 CONVERSION FACTORS FOR SENSITIVITY SETTING - MPF 2A

SENSITIVITY SETTING		1	2	3	4	5	6
INCREASE IN SENSITIVITY AT SETTING	1	-	0.33	0.09	0.03	0.01	0.004
	2	3.06	-	0.30	0.10	0.03	0.012
	3	10.31	3.37	-	0.35	0.11	0.04
	4	29.6	9.67	2.87	-	0.33	0.12
	5	89.9	29.4	8.72	3.04	-	0.36
	6	24.9	81.4	24.2	8.42	2.77	-

APPENDIX 5 ^{11}B N.M.R. SPECTROSCOPY. INSTRUMENTAL CONDITIONS

APPENDIX 5 ^{11}B n.m.r. SPECTROSCOPY - INSTRUMENTAL CONDITIONS

Two Fourier transform n.m.r. spectrometers were used in this work. The instrument at Wolverhampton Polytechnic used a conventional electromagnet giving a field of 1.88T. The ^{1}H resonance frequency was 80MHz. The high field, 9.4T, instrument at Warwick University used a superconducting magnet giving a ^{1}H resonance frequency of 400MHz. The corresponding spectrometer frequencies for recording ^{11}B spectra were 25.709MHz and 128.36MHz. In both instruments multinuclear probe heads with quadrature detection coils were used and field frequency stabilization was achieved by coupling the magnetic field to the resonance of deuterium oxide added to the boron chemical shift reference solution, (ie. internal hetero locking). The reference solution was contained in a 3mm diameter tube held concentric with a 10mm diameter sample tube by passing through the cap and a vortex spoiler. The annulus between the tubes was used to hold the solution being investigated. The samples were spun at about 20 r.p.s. to average out radial magnetic field gradients.

25.7MHz ^{11}B spectra of $10^{-2}M$ boric acid solutions in 95% v/v sulphuric acid, a sample showing a pronounced resonance from the $B(HSO_4)_4^-$ anion, showed considerable noise when the decay signal was transformed directly with no digital filtering. When the free induction decay signal was multiplied by an exponential function much of the noise was removed from the resulting spectrum, as the noise components are largely located in the tail of the FID signal.

The use of this technique usually enhances the signal to noise ratio at the expense of resolution if the line broadening factor introduced is greater than the intrinsic line width. Spectra were recorded with various specified values of line broadening but with the broad lines present in the ^{11}B spectra resolution was not adversly affected by line broadening values of up to 10Hz.

The resonances of the differing borate anions were not fully resolved at 25.7MHz. Spectra were recorded in which specified negative values of line broadening (ie. line narrowing) were combined with a gaussian multiplication of the FID as this procedure can give both increased resolution and reduction of noise. However, the resulting spectra obtained using various values of both parameters showed no improvement over those obtained using exponential multiplication of the FID.

The computer aquisition time,0.54 sec, of the 25.7MHz FID signal was long compared to ^{11}B relaxation times which are in the range 10 to 100 ms. The introduction of relaxation delays of up to 0.4 secs into the pulse repetition sequence produced no effect on the relative intensities of the $B(HSO_4)_4^-$ and aqueous boric acid peaks. The former relatively sharp resonance from a tetrahedrally symmetrical species would be expected to have the largest relaxation time of any of the species being investigated. The line intensities of the various resonances should therefore bear a true relationship to the concentration of the species involved.

The parameter set for the 25.7MHz ^{11}B n.m.r. spectra used in this work are given in the table - Figure A5.1. Similar considerations were applied when recording 128MHz spectra. The boron content of the glass in the probe head and the sample tube gave rise to a very broad 'background' resonance over the width of the n.m.r. spectrum with maximum intensity in the region of 0ppm shift.

When recording spectra at 25.7MHz the background was corrected after phase correction of the transformed data by subtracting a synthetic base line constructed from sine, exponential and/or polynomial functions. When using the high field instrument the base line was constructed by manual nomination of a number of points lying on the background it was desired to remove. If a low broad resonance arising from the sample is superimposed on the background, it may be impossible to separate the two when the background correction is made. This may possibly explain the anomolous spectra obtained in section 4.2.4, from chromotropic acid solutions in sulphuric acid.

FIGURE A5.1 PARAMETER SET FOR ^{11}B N.M.R.

Field	1.9T	9.4T
Spectrometer frequency	25.709MHz	128.360MHz
Observation offset frequency	4432Hz	50000Hz
Spectral width	15151Hz	10000Hz
Filter width	19000Hz	12500Hz
Block size	8k	4k
Aquisition time	.54s	.21s
Relaxation delay	.2 s	0s
Pulse width	7µs	12µs
Computer delay	16µs	25µs
Line broadening	10Hz	10Hz
Hz/pt	1.9	4.9
Hz/cm	51.4	128.4
ppm/cm	2	1

APPENDIX 6 REAGENTS USED

APPENDIX 6 REAGENTS USED IN THIS WORK

Boric acid Analar

Sodium carbonate, anhydrous. Analar

Sulphuric acid 98% w/w sg 1.84 Analar

Pure iron BCS 260/4 <0.0001%B

Stainless Steel BCS 463 <0.0003%B

In the fluorimetric work.

Resacetophenone G.P.R. recrystallized from dilute hydrochloric acid before use.

Thoron. The trisodium salt B.D.H. colorimetric reagent for thorium.

Arsenazo I. The trisodium salt p.a. Fluka.

Carboxyarsenazo III. The disodium salt p.a. Fluka.

Arsenazo III. The tetra sodium salt B.D.H.

For interference studies.

Chromium pellets, nickel sponge, cobalt powder, manganese flakes, titanium sponge, molybdenum powder, vanadium turnings, copper balls.

All the above Specpure. Johnson and Matthey. No boron detectable - less than 5ppm.

For n.m.r. work.

2-hydroxy-4-methoxybenzophenone 98% m.p. 63/65 Aldrich

2-hydroxy-4-methoxy-4'-methylbenzophenone "

2-hydroxy-4-methoxy-4'-chlorobenzophenone "

2,2'-dihydroxyazobenzene 98% Kodak

4 hydroxyazobenzene 98% m.p. 155/157 Aldrich

Chromotropic acid G.P.R.

Chromotrope 2R 75% Aldrich

SPADNS. The trisodium salt B.D.H.

Azomethine H B.D.H.

Sulphonazo III.The tetrasodium salt B.D.H.

REFERENCES

Chapter 1

1	Irvine,K.	J.I.S.I.	1957	186	54
2	Kapadia,B.M.,Brown,R.M. and Murphy,W.J.	Trans.A.I.M.E.	1968	242	1689
3	Lewellyn,D.T. and Cook,W.T.	Metals Tech.	1974	1	517
4	Melloy,G.F., Slimmon,P.R. and Podgursky,P.P.	Met.Trans.	1973	4	2279
5	Melloy,G.F. and Russ,J.C.	Met.Progr.	1966	90	82
6	Ridal,K.A. and Hughes,J.D.	J.I.S.I.	1967	205	183
7	Keown,S.R. and Pickering,F.B.	Metal Science	1977	Jly	225
8	Brande,W.T.	A manual of Chem.	1819	163	
9	Goward,G.W. and Wiederkehr,V.R.	Anal.Chem.	1963	35	1542
10	Hayes,M.R. and Metcalfe,J.	Analyst	1962	87	956
11	British Standard Handbook No.19 - Determination of Boron in Steel				
12	Schaak,M.F.	J.Sci.Chem.Ind.	1904	23	699
13	Low,W.H.	J.Am.Chem.Soc.	1908	28	807
14	Bode,J.D. and Fernando,Q.	Anal.Chem.	1960	32	277
15	Pasztor,L.C. and Bode,J.D.	Anal.Chim.Acta.	1961	24	467
16	Hobson,J.D.	B.I.S.R.A. Conf.Proc.	610/67		
17	Boltz,D.F. and Mellon,M.G.	Anal.Chem.	1966	38	321R
18	Golubtsova,R.B.	Zhur.Anal.Khim.	1960	15	481
19	Green,H.	J.B.C.I.R.A.	1962	10	56
20	Capelle,R.	Anal.Chim.Acta.	1961	24	555
21	Donnelly,D. MSc Thesis, The Polytechnic, Wolverhampton		1971		
22	Pickett,E.E. and Pau,J.C.M.	J.A.O.A.C.	1973	56	151
23	Agazzi,J.E.	Anal.Chem.	1967	39	233

24	Belcher,R.,Ghonaim,S.A. and Townshend,A.	Anal.Chim.Acta	1974	71	255
25	Boumans,P.W.	Mikrochim.Acta	1978		399
26	Lee,G.D.	MSc Thesis, The Polytechnic, Wolverhampton	1985		
27	White,C.E. and Hoffman,D.E.	Anal.Chem.	1957	29	1105
28	Sommer,L.	Chem.Listy.	1957	51	2032
29	Parker,C.A. and Barnes,W.J.	Analyst	1960	85	828
30	Babako,A.K. and Chalaya,Z.I.	Ukr.Khim.Zh.	1964	30	268
31	Babako,A.K. and Vasilevskaya,A.E.	Ukr.Khim.Zh.	1967	33	314
32	Pszonicki,L. and Tkacz,W.	Chemia.Analit.	1970	15	809
33	Nazarenko,V.A. and Vinkovetskaya,S.Ya.	J.Anal.Chem.USSR	1971	26	700
34	Bruce,T. and Ashley,R.W.	Rep.Atom.Eng.Can.	1973	AECL	4446
35	Gabriels,R. and Vankeirsbluck,W.	Lab.Pract.	1977	26	620
36	Hiraki,K.	Kinki Daigaka Rikogakuba Kenkya Hokoku	1975	10	23
37	Lapid,J.,Farhi,S. and Koresh,Y.	Anal.Lett.	1976	9	355
38	Gopala Rao,G. and Appalaraju,N.	Z.Anal.Chem.	1959	167	325
39	Monnier,D.,Marcantonatos,A and M.	Helv.Chim.Acta	1964	47	1980
40	Kristalev,P.V. and Chelnokova,M.N.	Z.Analit.Khim.	1974	29	1650
41	Marcantonatos,M. and A. and Monnier,D.	Helv.Chim.Acta	1965	48	194
42	Marcantonatos,M, Monnier,D. and Daniel,J.	Anal.Chim.Acta	1966	35	309
43	Monnier,D. and Marcantonatos,M.	Anal.Chim.Acta	1966	36	360
44	Monnier,D., Leibich,B. and Marcantonatos,M.	Z.Anal.Chem.	1969	247	188
45	Leibich,B., Monnier,D. and Marcantonatos,M.	Anal.Chim.Acta	1970	52	305

46 Monnier,D., Menzinger,C.A. and Marcantonatos,M.
Anal.Chim.Acta 1972 60 233

47 Afghan,B.K., Goulden,P.D. and Ryan,J.F.
Water Research 1972 6 1475

48 Marcantonatos,M., Gamba,G. and Monnier,D.
Helv.Chim.Acta 1969 52 538

49 Cook,E.B.T. and Holan,H. Nat.Inst.Met.S.Africa 1977 Rpt 1902

50 Holme,A. Acta.Chem.Scand. 1967 21 1679

51 Marcantonatos,M., Monnier,D. and Marcantonatos,A.
Helv.Chim.Acta 1964 47 705

52 Rigin,V.I. and Melrichenko,N.N.
Zav.Lab. 1967 33 3

Chapter 2

53 Neelakantam,K. and Ramachandra Rao,L.
Proc.Ind.Acad.Sci. 1947 5 81

54 Kamata,E., Goto,K. and Shibata,S.
J.Chromatog. 1975 115 660

55 Harrison,T.S. and Cobb,W.D. Analyst 1966 91 576

Chapter 3

56 Danielson,L. Talanta 1959 3 138

57 Langmyhr,F.J. and Skaar,D.B. Acta.Chem.Scand. 1959 13 2107

58 Langmyhr,F.J. and Arnesen,R.T.
Anal.Chim.Acta 1963 29 419

59 Brown,R.S. Can.J.Chem. 1964 42 2635

60 Langmyhr,F.J. and Holme,A. Anal.Chim.Acta 1966 35 220

61 Holme,A. and Langmyhr,F.J. Anal.Chim.Acta 1966 36 383

62 Brown,R.S. Anal.Chim.Acta 1970 50 157

63 Marcantonatos,M. and Leibrich,B.
Chimia 1970 24 447

64 Marcantonatos,M. and Menzinger,C.	Inorg.Chim.Acta	1975	14	227
65 Job,P.	Ann.Chim.Phys.	1928	9	113
66 Denison,R.B.	Trans.Farad.Soc.	1912	8	20
67 Klausen,K.S. and Langmyhr,F.J.	Anal.Chim.Acta	1963	28	335
68 Vosburgh,W.C. and Cooper,G.R.	J.Am.Chem.Soc.	1941	63	437
69 Freeman,D.C. and White,C.E.	J.Am.Chem.Soc.	1956	78	2678
70 Yoe,J.A. and Jones,A.L.	Anal.Chem.	1944	16	111
71 Harvey,A.E.and Manning,D.L.	J.Am.Chem.Soc.	1950	72	4438
72 Bent,H.E. and French,C.L.	J.Am.Chem.Soc.	1941	63	568
73 Asmus,E.	Z.Anal.Chem.	1960	178	104
74 Rose,N.S. and Drago,R.S.	J.Am.Chem.Soc.	1959	81	6138
75 Stearns,R.S. and Wheland,G.W.	J.Am.Chem.Soc.	1947	69	2025
76 Palmer,A.R.	Anal.Chim.Acta	1958	19	458
77 Shrivastawa,S.C.	Microchim.J.	1969	14	37
78 Gillespie,R.J. and Robinson,E.A.	Can.J.Chem.	1962	40	1009
79 Flowers,R.H. and Gillespie,R.J.	J.Chem.Soc.	1956		1925

Chapter 4

80 Antikainen,P.J. and Pitkamen,I.P.	Suomen Kemi.	1968	B41	65
81 Yasunobu,R.T. and Norris,E.R.	J.Biol.Chem.	1957	227	473
82 Oertel,R.P.	Inorg.Chem.	1972	11	544
83 Momii,R.K. and Nachtrieb,N.H.	Inorg.Chem.	1967	6	1189
84 Smith,Jr,H.D. and Wiersema,R.J.	Inorg.Chem.	1972	11	1152

85 Henderson,W.G., How,M.J., Kennedy,G.R. and Mooney,E.F.
Carbohyd.Res. 1973 28 1

86 Pasdeloup,M. and Brisson,C. Org.Mag.Res. 1981 16 164

87 Van Duin,M. Peters,J.A., Kieboom,A.P. and Van Bekkum,H.
Tetrahedron 1984 40 2901

88 Onak,T.P., Landesman,H., Williams,R.E. and Shapiro,I.
J.Phys.Chem. 1959 63 1533

89 Babcock,L. and Pizer,R. Inorg.Chem. 1980 19 56

90 Truhaut,R., Boudene,C. and Phu Lich,N.
Bull.Soc.Chim.(5e) 1966 8 2251

91 Wyatt,P.A.H. Trans.Farad.Soc. 1960 56 490

92 Kaandorp,A.W., Cerfontain,H. and Sixma,F.L.
Rec.Trav.Chim. 1962 81 969

93 Young,T.F. and Walrafen,G.E.
Trans.Farad.Soc. 1961 57 34

Chapter 5

94 Savvin,S.B., Kuzin,E.L. and Gribov, L.A.
Z.Anal.Khim. 1968 23 5

95 Savvin,S.B. and Kuzin,E.L. Talanta 1968 15 913

96 Perez-Bustamente,J.A. and Burriel-Marti,F.
Talanta 1971 18 717

97 Muk,A. and Savvin,S.B. Anal.Chim.Acta 1969 44 59

98 Tanner,D.W. and Bruice,T.C. J.Am.Chem.Soc. 1967 89 6954

99 Kuemmel,D.F. and Mellon,M.G.
Anal.Chem. 1957 29 378

100 Kuzin,E.L., Savvin,S.B. and Gribov,L.A.
Z.Anal.Khim. 1968 23 490